4D multiple-cathode ultrafast electron microscopy

John Spencer Baskin, Haihua Liu, and Ahmed H. Zewail[1]

Physical Biology Center for Ultrafast Science and Technology, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125

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Four-dimensional multiple-cathode ultrafast electron microscopy is developed to enable the capture of multiple images at ultrashort time intervals for a single microscopic dynamic process. The dynamic process is initiated in the specimen by one femtosecond light pulse and probed by multiple packets of electrons generated by one UV laser pulse impinging on multiple, spatially distinct, cathode surfaces. Each packet is distinctly recorded, with timing and detector location controlled by the cathode configuration. In the first demonstration, two packets of electrons on each image frame (of the CCD) probe different times, separated by 19 picoseconds, in the evolution of the diffraction of a gold film following femtosecond heating. Future elaborations of this concept to extend its capabilities and expand the range of applications of 4D ultrafast electron microscopy are discussed. The proof-of-principle demonstration reported here provides a path toward the imaging of irreversible ultrafast phenomena of materials, and opens the door to studies involving the single-frame capture of ultrafast dynamics using single-pump/multiple-probe, embedded stroboscopic imaging.

electron pulse generation | ultrafast imaging | irreversible dynamics

In 4D ultrafast electron microscopy (UEM), ultrafast light pulses generate electron packets by photoemission at the cathode of an electron microscope, and these are used to probe a dynamic process initiated by heating or exciting the microscopic specimen with a second, synchronized ultrafast light pulse (1, 2). In conventional implementations, each pump pulse on the specimen is accompanied by one suitably delayed laser pulse on the cathode to generate one packet of electrons probing a single time point in the evolution of the specimen. A record of the full course of temporal evolution of the specimen is then constructed by repeating the experiment multiple times with variation of the delay time between the two light pulses, reading out a separate CCD image for each delay time. Thus, information about different time points in the dynamic response of the specimen is obtained from different excitation events. This implementation is ideally suited for a specimen that undergoes irreversible but sufficiently well-defined dynamics to allow a new specimen area to be used for each time point (Fig. 1*A*), or for a specimen that recovers fully to allow repeated identical excitations of the same area (Fig. 1*B*); see also *Methodology*. The applications of these two approaches are numerous, as highlighted in a recent review account of the work (3).

For the study of completely nonrepetitive dynamics, for example, a stochastic process in a heterogeneous sample that does not return to its initial configuration, a series of snapshots following a single excitation event can provide the only direct and detailed view of the evolution. Observing the effects of a single excitation pulse with video-mode imaging can currently reach millisecond-scale time resolution, far short of the time scale for many phenomena of interest in nanoscale materials science, chemistry, and physics. Nanosecond resolution has been reached (4) by combining one excitation pulse with a train of light pulses on a single cathode, with deflection of the imaging electrons after passing the specimen plane to direct each successive pulse to a new region of the detector (Fig. 1*C*). This nanosecond method has been successfully used with a high-speed electrostatic deflector array to obtain time sequences of irreversible and stochastic processes (5, 6).

Here we demonstrate a technique that removes any limit on time resolution imposed by image deflection and in a single frame enables the capture of ultrafast phenomena. With this approach, it is possible to probe and distinctly record multiple time points in a dynamic process following a single initiation pulse. The probing electron packets are all generated by a single light pulse that impinges on multiple, spatially distinct, cathode surfaces (Fig. 1*D*). Time separations between packets in the electron-pulse train are adjusted by the cathode spatial and electrostatic configuration. In the present application, two electron packets, generated from two source locations at the same potential and separated in time by 19 picoseconds (ps), are recorded on each CCD frame after undergoing diffraction in a gold film following femtosecond heating. The packets originate from different cathode locations, pass through the same area of the specimen, and are recorded at distinct locations on the detector, thereby encoding two different time points in the evolution of the specimen. The results obtained provide the basis for exploration of expanded application of the multiple-cathode concept.

Methodology

Fig. 1 illustrates the concept of the multiple-cathode approach, in the context of other established implementations of laser-based time-resolved microscopy. In each of the four panels of Fig. 1, the principal UEM elements are shown: an electron photoemission source (cathode) and a specimen, with optical access to each for laser irradiation, and a detector. Fig. 1 *A* and *B* contrast basic options available for data acquisition, while Fig. 1 *C* and *D* represent multiple-probe methods distinguished by the number of light pulses on the cathode and the manner of image separation on the detector.

In this laboratory, both the single-pulse and stroboscopic techniques have been used extensively. When a specimen irreversibly changes following the pump laser excitation, an image

Significance

Imaging of dynamical processes in materials and biological structures requires resolutions in both space and time. Four-dimensional electron microscopy was developed to image microscopic objects down to the atomic-scale spatial resolution and the femtosecond time resolution. Unlike stroboscopic techniques applied in studies of reversible processes on the femtosecond scale, single-pulse methods have been limited to the nanosecond scale for capturing irreversible processes such as materials phase transformations. In this contribution, we report on 4D multiple-cathode ultrafast electron microscopy, which enables the direct capture with femtosecond time resolution of phenomena at multiple times in their dynamics and in a single frame. The scope of applications is wide ranging.

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[1]To whom correspondence should be addressed. Email: zewail@caltech.edu.

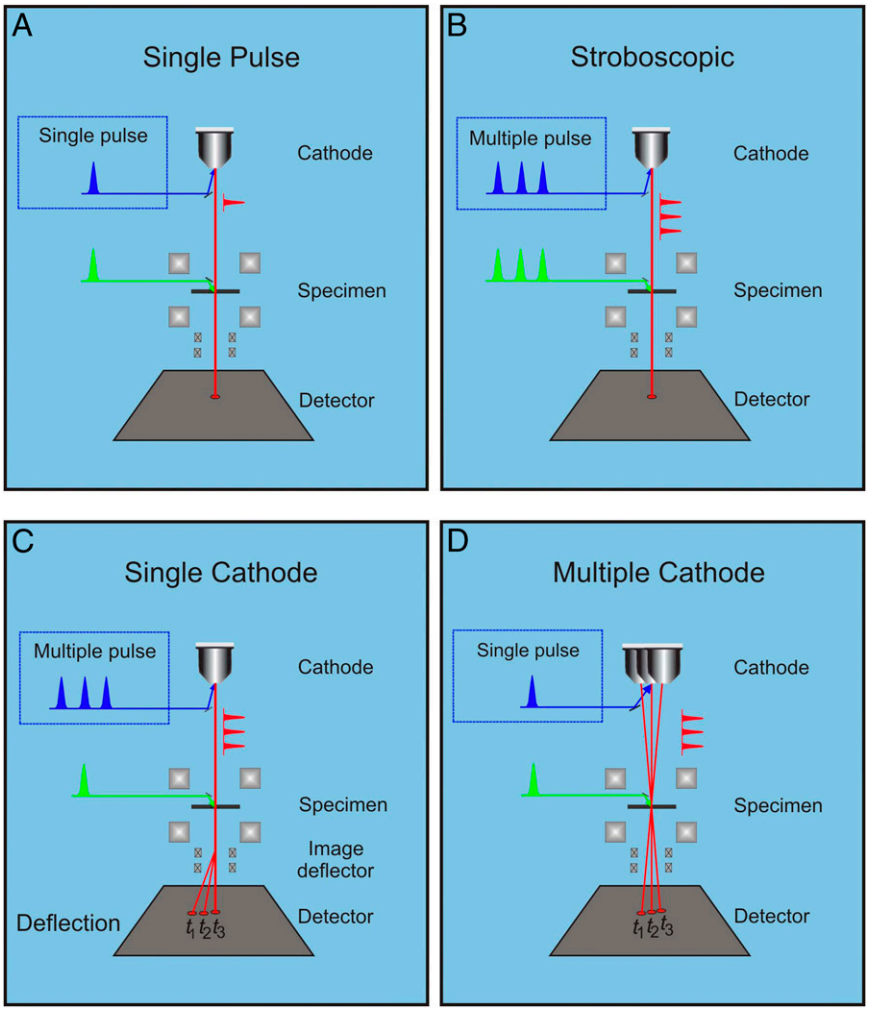

Fig. 1. Variant implementations of UEM. (*A*) Single-pulse UEM, which enables single-shot imaging of homogeneous specimens. (*B*) Stroboscopic UEM. (*D*) Multiple-cathode UEM. For comparison, we include, in *C*, the single-cathode, deflection method. See text for details.

(real space or diffraction) for a single time point can be acquired using the single-pulse method of one pump pulse and one electron pulse, after which the detector frame is read out (Fig. 1*A*). For a homogeneous specimen, the experiments may be repeated at different time delays and on different specimen locations to achieve the equivalent of a full "single-shot" transient. When, instead, conditions of repeatability are met, acquisition of a single image for a single time delay may also be carried out stroboscopically as illustrated in Fig. 1*B*, in which identical pump/probe cycles are simply repeated as many times as required to accumulate a single image frame of the desired quality before detector readout (Fig. 1*B*). Additional time points can be acquired at the same specimen location. Both acquisition modes have thus far been used in this laboratory with only a single probe pulse per excitation, as shown. The time resolution achieved with the stroboscopic method took microscopy into the femtosecond regime, while in the single-pulse recording, hitherto, the resolution was typically on the nanosecond scale.

Two single-pump/multiple-probe techniques are also illustrated in Fig. 1. The single-cathode variation (Fig. 1*C*) is implemented by directing a train of timed laser pulses on the cathode to generate a train of electron packets for every excitation pulse. These electron packets probe a series of different times in the course of specimen dynamics and must then be individually deflected to distinct locations on the detector using fast switching electronics. The nanosecond time resolution is associated with this deflection approach.

In the multiple-cathode technique of Fig. 1*D*, which is distinguished by the ultrafast time scale accessible for imaging, a high precision in image timing and location on the detector are intrinsic features of the methodology. Here, one laser pulse to both the specimen and cathodes is accompanied by a train of temporally spaced electron pulses, with each from a distinct cathode surface. The timing of the pulses is controlled by the source locations and electrostatic potential environments, while, in the basic implementation illustrated, the separation of image locations depends largely on the lateral spatial separation of the sources. This arrangement has a direct analogy in time-resolved optical spectroscopy to the use of reflective echelon steps (used by one of us, A.H.Z.) to produce from one incident light pulse a train of time-delayed light pulses that can be separately detected after passing a sample in consequence of the spatial offset of the step sources (ref. 7 and references therein). A means for further static separation of the UEM images is discussed below.

A more detailed view of multiple-cathode probing in our second-generation UEM apparatus is shown in Fig. 2. Fig. 2*A* depicts the 200-keV microscope column, modified to admit separate laser irradiation of the specimen and of a hybrid field emission gun (FEG) cathode (8). A significant feature shown

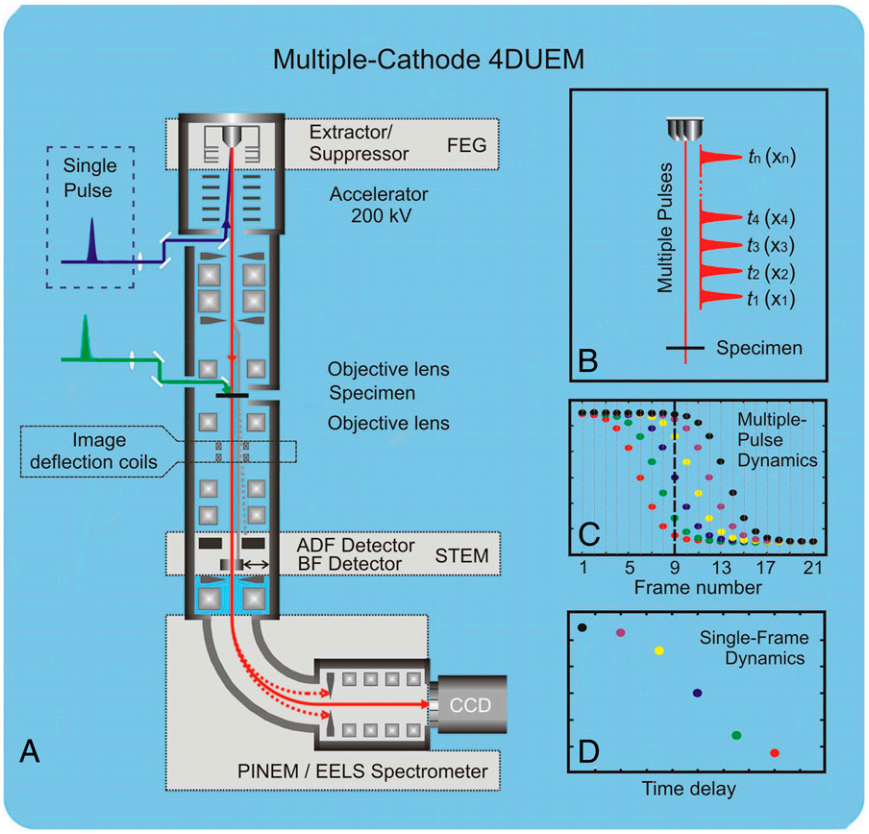

Fig. 2. Multiple-cathode UEM. (*A*) A schematic representation of the essential elements of the 4D microscope with energy filtering. Synchronized femtosecond laser pulses are focused on the cathode and on the specimen for UEM operation. ADF, annular dark field; BF, bright field; STEM, scanning transmission electron microscopy. (*B*) A train of electron packets with different arrival times t_i is generated by a single UV laser pulse at multiple, spatially separate cathode positions (x_i). (*C*) Data from a thought experiment in which multiple-cathode UEM measurement displays a drop in a signal (diffraction or image) intensity following laser excitation. Six electron packets equally separated in time probe the specimen for each excitation, and the signals from each packet are plotted for a series of frames recorded for increasing time delay between the specimen and cathode excitation laser pulses. Signals from the first and last packets to reach the specimen are represented by the black and red circles, respectively. (*D*) Data from the six packets of a single frame (frame 9) of *C* are plotted on a time axis that accounts for the relative timing of the packets, thus providing a temporal record of essentially the full transition dynamics.

here but not in Fig. 1 is the magnetic sector that directs the electron beam through a 90° turn to reach the CCD camera, providing the capability of electron energy loss spectroscopy (EELS) or photon-induced near-field electron microscopy (PINEM) (9). Another significant feature of the design is the optical arrangement for precision control of the excitation pulse on the specimen, detailed in ref. 10. The femtosecond UV and green light pulses that are directed to the cathode and specimen, respectively, are generated from a single infrared laser source operating at a user-selectable repetition rate. The green beam passes through a variable optical delay path to adjust the relative timing of the pulses before their arrival at the microscope. Electrons are recorded by a 2048 × 2048 pixel CCD.

In Fig. 2 *B*–*D*, the concept of multiple-cathode operation is illustrated with a thought experiment. Shown in Fig. 2*B* is a train of electron packets generated by a single UV pulse and designated by the time sequence t_1 to t_n, with each arising from a separate cathode location, as indicated by coordinates x_1 to x_n. Each electron packet follows its own path down the column to the specimen area under investigation, and is afterward detected at a separate area on the CCD. Fig. 2*C* illustrates data from an "in principle" measurement in which a specimen displays a drop in a signal value following laser excitation. Six electron packets equally separated in time probe the specimen for each excitation, and are recorded in a single image frame. The signals from each of the six packets in a given frame are plotted at the *x* coordinate corresponding to that frame for a series of frames recorded for increasing time delay between the laser pulses for specimen and cathode irradiation. Signals from the first and last packets to reach the specimen are represented by the black and red circles, respectively. The signals recorded by the six packets in the ninth frame of Fig. 2*C* are plotted in Fig. 2*D* on a time axis that accounts for the time delays between the packets. A temporal record of essentially the full transition dynamics of the specimen is thus obtained from that single frame.

For an experimental implementation of this concept, an 11-nm-thick oriented gold crystal film on a copper grid was excited by femtosecond pulses of 519-nm light at a fluence of 1.6 mJ/cm^2. The two electron beams were generated at the center flat of a conical lanthanum hexaboride (LaB_6) cathode (90° cone angle) and at one projecting corner of its mounting base. The distribution of electron counts between the two packets was balanced by control of the UV beam alignment and gun tilt. The electron beams were incident on the specimen along the gold [100] zone axis.

Results

Results from the demonstration experiments are presented in Figs. 3 and 4. Shown in Fig. 3*A* are the images on the detector of the two electron beams corresponding to the two packets generated by each UV laser pulse. The labels "center" and "side" refer to the source location on the cathode. In Fig. 3*B*, the beams

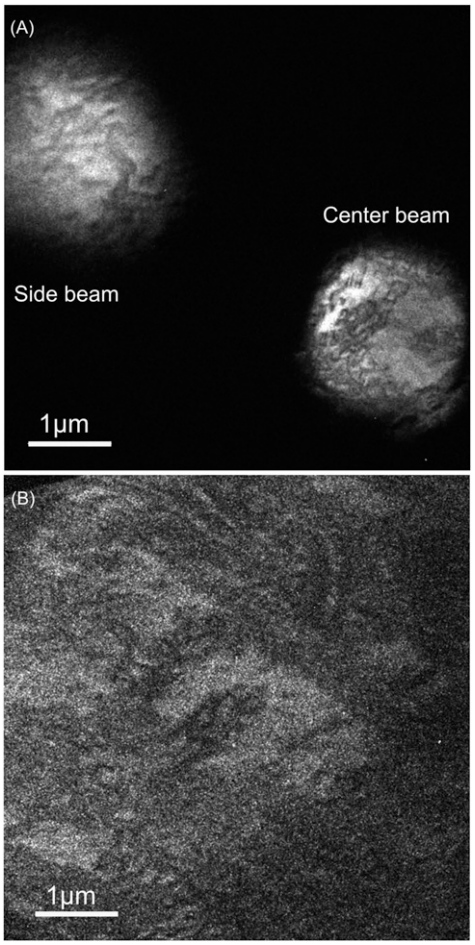

Fig. 3. Images from a two-cathode experiment. (*A*) Gold film illuminated by two pulsed electron beams generated by photoemission at two locations on the cathode, as indicated. (*B*) The same beams as *A* after spreading their intensity to uniformly cover the area of study (center of the image).

are spread to overlap on the specimen area of interest. During collection of data, a selected-area aperture was used to select only the central region of Fig. 3*B* illuminated uniformly by each of the beams. The diffraction pattern obtained from this specimen region under these conditions is shown in Fig. 4*A* with a distinct set of peaks for each of the two beams. For this particular alignment regime, the side beam, identified by the red circles in Fig. 4*A*, was the more intense of the two.

A series of experiments was performed in which the relative delay of the excitation and probe laser was scanned. For each recorded frame, the average integrated intensity was evaluated for the eight {042} peaks in the diffraction pattern associated with each of the beams. The values obtained for the center and side beam peaks in a given frame were normalized by their respective (000) intensities and scaled to set the average value from the first 25 frames to one. Center and side beam data from a given frame are plotted on the same vertical line in Fig. 4*B*, i.e., following the same format as Fig. 2*C*. Here, however, two time axes have been added, and these will be explained below.

The diffraction intensities of both electron beams show an abrupt drop in moving from left to right in Fig. 4*B*, i.e., as the probe laser delay increases. The form of this change for both beams matches well that revealed in previous similar experiments on gold (11, 12). However, the change in side beam intensity clearly occurs earlier in the sequence of frames than that of the center beam. The signal evolution for each beam has been fit with a single exponential drop to a lower metastable value on the time scale of the plot, and the fit curves are shown as red and green solid lines. The onset of the change in these fits has been used to fix the zero points on the two time axes and to determine that the time separation of the two probing electron packets is 19 ps. With this knowledge, the green and red time axes have been added, and these indicate, for any given frame, the arrival time at the specimen of the center and side packets, respectively, relative to the excitation pulse. Note that the packet originating from the side arrives later in time, as can be seen from the fact that, for any frame between the zero points of the red and green time axes, only the side beam observes a specimen that has already been excited (positive time).

Discussion

The multiple-cathode concept was developed to provide the means for the generation of a sequence of ultrafast probe pulses that can unambiguously track a specimen's response to a given excitation pulse. This approach is fundamentally different from

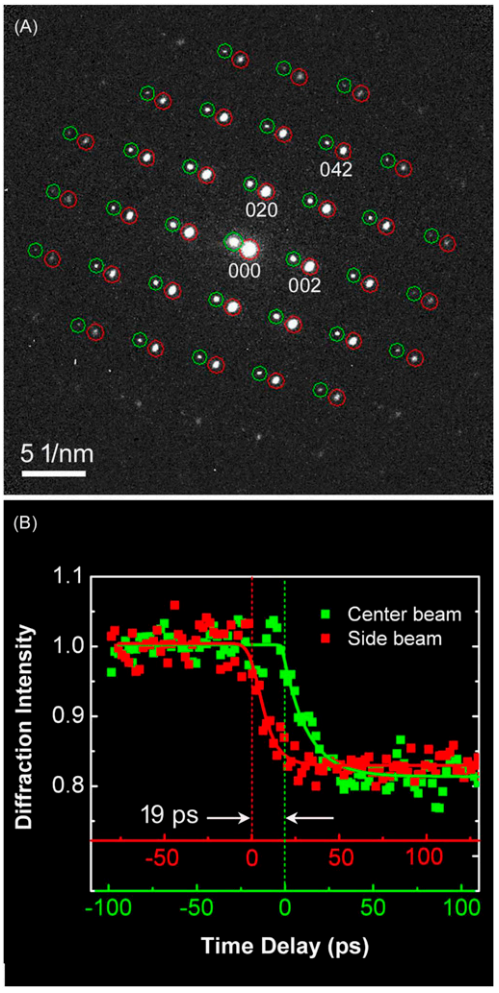

Fig. 4. Diffraction from a two-cathode experiment. (*A*) Diffraction patterns of an oriented gold crystal film from two pulsed electron beams, under conditions shown in Fig. 3*B*. The green and red circles indicate peaks from the center and side beams, respectively. (*B*) Dynamics of the diffraction intensity recorded by scanning the laser time delay. Data from the two electron packets are plotted in green and red, probing two time delays in each frame. The lower-intensity center beam data have been filtered to remove high-frequency noise. Fits of the time evolution of each transient yield the indicated time separation of 19 ps.

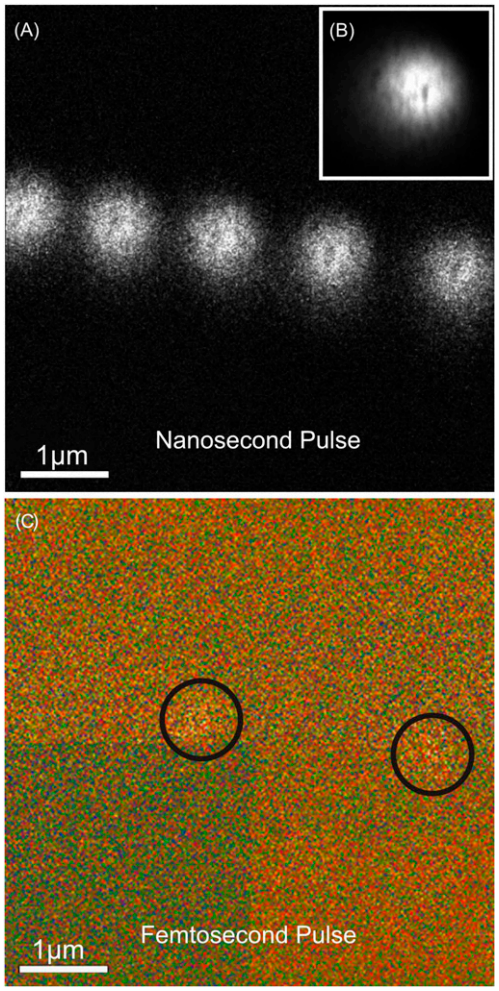

Fig. 5. Single cathode, multiple probe in UEM. (*A*) A time sequence of images on a single frame. The images of one area of an aluminum film are produced by a train of nanosecond electron packets generated by laser irradiation, at a 50-Hz repetition rate, of a single cathode. The electron beam after the specimen is swept by the image deflection coils to send each packet to a separate spot on the detector; at the repetition rate used, the time separation between images is 20 ms. (*B*) Stroboscopic UEM image of the aluminum film of *A* recorded by acquiring a total of 150 of the nanosecond electron packets. (*C*) Two single-laser-shot electron packets, produced from a single cathode by repetitive femtosecond UV laser irradiation at 200 kHz, are detected on a single frame. The images were separated by the image deflection coils with a modified control circuit.

that of the single cathode with electron packet deflection illustrated in Fig. 1*C*. Because the electron packets in the single-cathode method are not generated with a spatial separation, they must be deflected after the specimen to separate areas of the detector whenever the packet interval is shorter than the camera readout time. An example of this imaging method is provided by the result in Fig. 5*A* of a slow sweep of nanosecond-length single-shot packets repeatedly imaging one area of an aluminum film in our microscope. (The same area of the film is shown in Fig. 5*B* as recorded by stroboscopic UEM imaging.)

A thoroughly optimized implementation of this multiprobe technique that uses an arbitrary waveform generator laser, a modified column for nanosecond high-electron-count single-shot packet throughput, and a high-speed electrostatic deflector array after the sample has been reported to be capable of separately recording nine packets in a train with intervals above 25 ns (5, 6). We investigated the possibility of using the standard image deflection coils in our microscope, with modified electronic control, for sweeping femtosecond single-shot packets, as in Fig. 5*C*, and found that packets at intervals no shorter than hundreds of nanoseconds could be accommodated.

In contrast, we have demonstrated here that the multiple-cathode method can provide much shorter probe packet intervals with extremely stable timing and image spatial separation without major modifications to the standard microscope column configuration. The timing and image location in the conducted experiments are fixed by the standard cathode spatial configuration, with the packet that travels a longer distance arriving later. It is our expectation that a specially designed cathode structure with a set of displaced emitting surfaces should be able to provide a train of electron packets that will each arrive at the specimen at a different time and will be spatially separated at the detector (see below). The timing differential should be strongly dependent on the earliest stage of electron acceleration at each surface and may be adjustable to a significant extent by variation of the applied extraction fields, allowing additional control of experimental conditions. Given the longitudinal spatial separation of micrometers to millimeters that could be designed, we see the potential to generate multiple, ultrafast electron packets separated by femtosecond to picosecond delays in single-frame imaging, subject only to pulse-width limitations.

Here, the source spatial configuration provided the requisite spatial separation; however, in images such as those in Fig. 3 *A* and *B*, the displacement on the detector between the dual images of a given specimen location was only about half as large, measured in pixels, as that between the diffraction peaks. To expand the range of applications to high-resolution imaging, a larger separation of source points could increase the image separation, but additionally, we propose to establish a voltage differential between cathodes by incorporating voltage-dividing resistances within the design of the multisurface cathode. The packets of slightly different energy will then be focused to different spots on the detector as a consequence of the energy dispersion of the magnetic sector. The energy differences designed to space the train of images across the detector will also affect the packet's timing because of their different drift speeds, but this timing effect is not expected to be a major factor. For example, a change in electron energy of 1000 V results in a change in the ~4-ns flight time from cathode to specimen of only 6 ps in our 200-keV microscope.

With the current conventional cathode used (low quantum efficiency), the electron count in single packets of the femtosecond mode, as seen in Fig. 5*C*, is too low for single-shot imaging or diffraction, but here, stroboscopic acquisition of data were combined with the multiple-packet recording of a single frame. (Strategies for achieving high electron counts in ultrashort packets are under active research.) In the demonstration made here on gold, use of multiple probe packets was found to be useful in relaxing the requirement of reversible dynamics. This is true because the gold film, like most samples, tends to be modified more or less quickly by repetitive excitation. Such progressive permanent changes can easily compromise the interpretation of data acquired in the conventional sequential manner. In contrast, multiprobe techniques ensure that the signals measured at each of the time points contained within a single frame correspond to exactly the same specimen condition, and are therefore internally consistent, without a requirement for long-term reversibility. We envision that multiple-cathode operation can be profitably embedded with stroboscopic measurement, and its implementation will clearly provide a many-fold increase in the efficiency of all UEM measurements, while extending UEM applications into the currently inaccessible realm of materials undergoing rapid modifications.

Conclusions

In this contribution, the multiple-cathode technique is introduced for expanding the domain of UEM studies. The concept has been

described, and the results of a proof-of-principle demonstration were presented. Electron packets generated at spatially distinct cathode locations probed distinct time points in a dynamic process initiated by a single femtosecond specimen initiation pulse in UEM. The static nature of the electrostatic environment ensures stable image location and ultrafast timing precision. The importance of this approach is in obtaining "all-at-once" imaging, with ultrashort time separations, in a single frame at a specific specimen location. To realize the full power of the concept described here, design of a cathode with multiple emitting surfaces is planned, allowing rapid capture of ultrafast dynamics in all types of specimen, from those undergoing reversible dynamics, to materials under conditions where laser damage is possible, to stochastic processes in single-shot (picosecond or femtosecond) studies. For a design allowing the separate emitting surfaces to be operated at distinct voltages, ultrafast multiple-probe imaging can be performed with spatial separation of the images on the detector by means of electron energy dispersion in the magnetic sector. The technique may also be combined with EELS, and the potential of multiple cathodes in PINEM (8) is of interest to us and shall be explored in further experiments.

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1. Zewail AH, Thomas JM (2010) *4D Electron Microscopy: Imaging in Space and Time* (Imperial College Press, London).
2. Zewail AH (2010) Four-dimensional electron microscopy. *Science* 328(5975):187–193.
3. Flannigan DJ, Zewail AH (2012) 4D electron microscopy: Principles and applications. *Acc Chem Res* 45(10):1828–1839.
4. Bostanjoglo O (2002) High-speed electron microscopy. *Advances in Imaging and Electron Physics*, eds Hawkes P, Kazan B, Mulvey T (Elsevier, New York), Vol 121, pp 1–51.
5. LaGrange T, et al. (2012) Approaches for ultrafast imaging of transient materials processes in the transmission electron microscope. *Micron* 43(11):1108–1120.
6. Santala MK, et al. (2013) Irreversible reactions studied with nanosecond transmission electron microscopy movies: Laser crystallization of phase change materials. *Appl Phys Lett* 102(17):174105.
7. Shapiro SL, ed (1977) *Ultrashort Light Pulses–Picosecond Techniques and Applications*, Topics in Applied Physics (Springer, Berlin), Vol. 18.
8. Park HS, Baskin JS, Kwon OH, Zewail AH (2007) Atomic-scale imaging in real and energy space developed in ultrafast electron microscopy. *Nano Lett* 7(9):2545–2551.
9. Barwick B, Flannigan DJ, Zewail AH (2009) Photon-induced near-field electron microscopy. *Nature* 462(7275):902–906.
10. Zewail AH, Baskin JS (2014) US Patent Appl 2014/0131574 A1.
11. Barwick B, Park HS, Kwon OH, Baskin JS, Zewail AH (2008) 4D imaging of transient structures and morphologies in ultrafast electron microscopy. *Science* 322(5905):1227–1231.
12. Park HS, Baskin JS, Barwick B, Kwon OH, Zewail AH (2009) 4D ultrafast electron microscopy: Imaging of atomic motions, acoustic resonances, and moiré fringe dynamics. *Ultramicroscopy* 110(1):7–19.