

## Femtosecond electron diffraction for direct measurement of ultrafast atomic motions

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We have developed a femtosecond electron diffraction system capable of directly measuring the complete transient structures with atomic level detail and on 400-fs time scale in solid materials. Additionally, a diffraction image with significant signal-to-noise ratio to reveal the long-range order can be obtained with a single electron pulse of 700 fs in duration. A direct observation of ultrafast lattice expansion following the irradiation of femtosecond pulsed laser of Ag film has been demonstrated. © 2003 American Institute of Physics. [DOI: 10.1063/1.1593831]

Atomic motions on the fundamental time scale of a single atomic vibrational period (100 fs to  $\sim 1$  ps) ultimately determine the evolution of new phases in solids, the kinetic pathways of chemical reactions, and the biological functioning processes. Techniques for direct observation of these structural dynamics on this fundamental time scale are being developed utilizing time-resolved diffraction with both pulsed x-ray and electron beams. Currently, time-resolved x-ray diffraction has been the primary choice, and several ways of generating ultrashort hard x-ray pulses to perform diffraction experiments have been demonstrated.<sup>1-9</sup> However, due to the relatively weak probe beam intensity, most of the experiments done so far with x-ray diffraction have been restricted to the measurement of a single rocking curve, which provides only limited information of atomic motions within the unit cell.

In contrast, time-resolved electron diffraction (TRED) provides an unique opportunity for a complete determination of the transient structures with atomic level detail under this low probe intensity condition, since the atomic elastic scattering cross sections of electrons are about five orders of magnitude greater than those of x rays. TRED has been used to study solid phase transitions,<sup>10</sup> determine the structures of transient species in gas phase,<sup>11-14</sup> and follow surface dynamics.<sup>15,16</sup> Up to now, TRED experiments have all been confined to the time scale of a few picoseconds.

To directly measure the structural dynamics at the femtosecond temporal resolution with ED, several major challenges must be surmounted. They include generation of femtosecond electron pulses with sufficient beam intensity, measurement of electron pulse width with femtosecond accuracy, and precise determination of the time zero where electron and laser pulses are temporally overlapped with each other. To this end, we have developed a femtosecond electron diffraction (FED) system with the capability of complete determination of the transient structures with atomic level detail and on a few hundred femtosecond time scale in solid materials. This time resolution is close to an order of magnitude shorter than previously published work.<sup>12</sup>

The FED apparatus consists of four major components:

an amplified femtosecond laser system, a femtosecond pulsed electron gun, a diffraction imaging system, and a streak camera. An all diode-pumped, amplified Ti:sapphire laser system is used for FED. It produces sub-50-fs pulses, with wavelength tuning range of 780 to 820 nm and adjustable repetition rate of a few Hz to up to 10 kHz. The output pulse energy is more than 900  $\mu\text{J}$  at a 1-kHz repetition rate.

To probe the ultrafast structural dynamics, the temporal width of the probe electron beam has to be shorter than or at least comparable to the time scale of processes under investigation. Additionally, it must maintain the highest possible beam intensity to record the detailed transient structural changes, preferably with the capability of capturing the transient structure with a single femtosecond electron pulse. However, space-charge and other non-space-charge (NSC) broadening effects act to broaden the electron pulse as it propagates. The SC effect is the self-dispersion due to the Coulomb repulsion between electrons in a pulse, which is most significant when the electron density is high. NSC broadening occurs due to the initial photoelectron energy distribution and different traveling times of electrons along different trajectories. These effects on the temporal resolution of streak camera have been discussed in detail in literature.<sup>17-19</sup> NSC broadening that occurs during the initial acceleration of the electrons away from the photocathode (PC) to extraction mesh is most significant, since this is the region where electrons have least kinetic energy. This broadening can be reduced to less than 200-fs by applying extracting field larger than 12000 kV/m and reducing the initial electron energy distribution to less than 0.5 eV.<sup>18</sup> NSC broadening in the post-extraction region can be essentially removed by using a small pinhole to limit e-beam size (diameter less than 500  $\mu\text{m}$ ), magnetic lens, and high electron-beam energy.

It has been shown<sup>20,21</sup> that the SC effect is unavoidable in the high beam intensity regime required for femtosecond ED experiment. To minimize this broadening, a highest possible extraction field at the PC is necessary to accelerate nascent photoelectrons and spread them out longitudinally across space to weaken the Coulomb interactions. Additionally, the SC broadening in the post-extraction region can be mitigated by using higher beam energy, minimizing the

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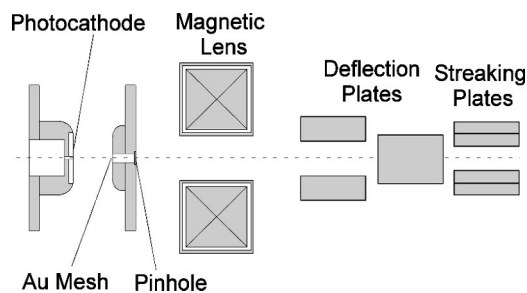


FIG. 1. Schematic of femtosecond electron gun used in FED system.

travel distance from PC to sample, and using magnetic lenses where the electron velocities remain unchanged during focusing.

The femtosecond electron gun developed for FED (Fig. 1) follows these considerations. The electron pulses, generated through photoemission from a back-illuminated PC (450-Å Ag film on a Sapphire disk) with frequency-tripled (266 nm) femtosecond laser pulses, are accelerated to 60 keV through an extraction electric field of 12000 kV/m between PC and extraction mesh. After extraction, the electron pulses are reshaped in size by a 150- $\mu\text{m}$  pinhole, collimated with a home-made magnetic lens, and positioned to the sample by a pair of deflection plates for diffraction measurements. Compared with the initial electron gun,<sup>22</sup> both the extraction electric-field strength and beam energy have been doubled in our second-generation electron gun by redesigning the geometry of PC and extraction assembly, and by careful polishing of their surfaces. As a result, its performance has been significantly improved. Given the same beam intensity, electron beams with better collimation and smaller beam size are produced, which results in longer spatial coherence and finer diffraction images. Most important of all, the beam intensity is more than doubled for a given pulse width. The gun can deliver  $\sim 2000$  electrons with pulse width less than 300 fs (see Fig. 2), which makes it possible to perform subpicosecond single-shot experiments to study ultrafast melting in solids.

The ED images are recorded with a two-dimensional imaging system composed of a Chevron-type microchannel plate (MCP), a P11 phosphor screen on an optical-fiber faceplate, and a 12-bit, thermoelectrically cooled CCD camera of 1.3 megapixels. The spatial resolution of this imaging system is mostly determined by the MCP detector and is estimated

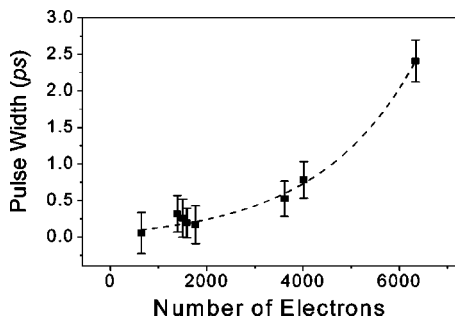


FIG. 2. Electron pulse width as a function of number of electrons per pulse of the 60-keV electron gun. The streak speed was calibrated by sending two electron pulses, separated in time by a well-defined 66.7 ps, through the electron gun during each streak measurement. The error bars represent the resolution of 250 fs/pixel ( $\sim 1.3 \times 10^8$  m/s).

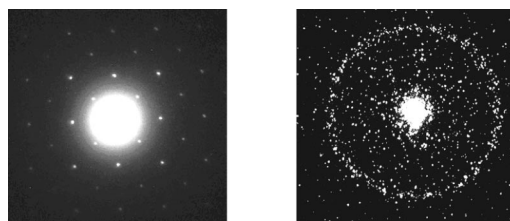


FIG. 3. Left panel: Diffraction image of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  in [100] direction recorded with  $\sim 4 \times 10^7$  electrons. Right panel: Diffraction image of 400-Å Al film taken with a single electron pulse with  $\sim 4000$  electrons ( $\sim 700$  fs). The ring in the image corresponds to the (220) Bragg peak. Each bright spot in the images represents a single detected electron.

to be better than 40  $\mu\text{m}$ . This resolution enables us to measure less than 0.5% lattice change with a 60-keV electron beam. The detector gain depends on the MCP bias and the acceleration voltage from the exit of MCP to the phosphor screen, and can be set in low gain mode with bigger dynamic range for long integration, or in high gain mode for a single-shot experiment.

A streak camera is also incorporated in the electron gun (see Fig. 1 for streaking plates), for doing a single-shot measurement of the electron pulse. An average streaking speed better than 250 fs/pixel ( $\sim 1.3 \times 10^8$  m/s) for 60-kV electron beams has been obtained by applying a  $\sim 5.5$  kV/ns voltage ramp across the streaking plates triggered by a pair of GaAs photoconductive switches. The temporal width of electron pulses as a function of electron numbers per pulse in the low beam intensity regime is plotted in Fig. 2. The SC effect is immediately clear at high beam intensity with more than several thousand electrons per pulse, where the electron pulse width shows strong dependence on the beam intensity. At low beam intensity with fewer than 2000 electrons per pulse, the pulse durations are less than 300 fs, comparable to the temporal resolution of 250 fs in the streaking experiment, and do not show any significant intensity dependence. This implies that pulses with durations less than 250 fs can be generated with fewer than 1000 electrons per pulse in this NSC limited regime.

The overall temporal resolution  $\tau_{\text{total}}$  in the FED experiment is set by several factors, and can be estimated as

$$\tau_{\text{total}}^2 = \tau_{\text{pump}}^2 + \tau_{\text{probe}}^2 + \tau_{\text{mismatch}}^2 \quad (1)$$

where  $\tau_{\text{pump}}$  and  $\tau_{\text{probe}}$  are pump laser and probe electron pulse width, respectively, and  $\tau_{\text{mismatch}}$  is the temporal mismatch at the sample surface arising from the geometrical arrangements of pump and probe pulses. For a near-collinear arrangement of excitation laser and probe electron pulses with cross angle less than  $10^\circ$  and 350- $\mu\text{m}$  electron beam size, the  $\tau_{\text{mismatch}}$  is estimated to be  $\sim 200$  fs in our experiment. Therefore, the  $\tau_{\text{total}}$  for a 300-fs electron pulse is less than 400 fs.

With the developed FED system, a high-quality diffraction image comparable to that of commercial transmission electron microscope (left panel in Fig. 3) can be obtained with a few million electrons (e.g., 20-s integration time with 2000 electrons/pulse at 1 kHz). However, for irreversible structural changes in solids, determining transient structures with a single electron pulse is required. As shown in the right panel of Fig. 3, a diffraction image with a large enough signal-to-noise ratio to reveal the long-range lattice order can

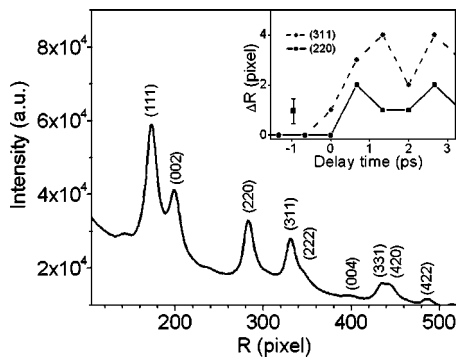


FIG. 4. A static diffraction intensity curve as a function of diffraction angle (pixel distance from the center beam) from a 400-Å Ag film recorded with the FED system. Inset: The shift of Bragg peaks of (220) and (311) as a function of delay time after femtosecond laser excitation at fluence of  $6 \text{ mJ/cm}^2$ . The time step is 600 fs.

be obtained with only  $\sim 4000$  electrons or less. This sets the upper limit of temporal resolution for single-shot experiments to study ultrafast order–disorder transitions, such as melting, at  $\sim 700$  fs.

The properties of metals following the irradiation of the ultrafast pulsed laser have been studied extensively with optical probes.<sup>23,24</sup> These optical measurements indicate that the lattice heating resulted from strong electron–phonon coupling is ultrafast in a couple of picosecond time scale. A direct measurement of this lattice heating has been performed with the developed FED. In the experiment, a 400-Å Ag film was excited by a femtosecond pulsed laser at a relatively low fluence of  $6 \text{ mJ/cm}^2$  to avoid any sample damage from melting. The electron number of each probe pulse was kept below 2000 to maintain the overall temporal resolution better than 400 fs. Upon femtosecond laser excitation, a concerted motion of Bragg peaks was observed, where all Bragg peaks start to shrink to a center zero-order spot and reach maximum shift, which corresponds to  $\sim 1\%$  expansion of lattice spacing, in about 2 ps (Fig. 4). This time scale is the same as that of electron–phonon thermalization observed in optical measurements. Additionally, it is found that the amplitude of peak shift is proportional to its original pixel position (diffraction angle), which is a clear indication of isotropic lattice expansion resulted from the laser heating.

In conclusion, we have developed a FED system for direct measurement of the transient structures. For laser-induced reversible structural changes, the FED can be operated at kHz repetition rate and in non-space-charge limited regime with 2000 or fewer electrons per pulse. The corresponding temporal resolution is better than 400 fs. The diffraction images at each delay time can be integrated over time for an optimal signal-to-noise ratio for the complete determination of transient structures. For nonreversible structural changes, by recording diffraction images with a single femtosecond electron pulse, a temporal resolution of  $\sim 700$  fs can be retained to measure order–disorder structural

changes. We believe that the capability of FED in recording complete diffraction images on the femtosecond time scale, instead of measuring just a single rocking curve, represents a significant step forward in direct determination of transient structures. This ability makes possible the measurement of detailed atomic motion in a unit cell.

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