Applications of Femtosecond Electron Microscopy/Diffraction

Jau Tang
Research Fellow and Deputy Director
Research Center for Applied Sciences

During most of the periods of human civilization, men perceive nature and its changes through their sensory organs such as eyes and ears. For six thousand years ever since the first written record of men, the timing of human activities with natural clocks based on periodic events of heavenly bodies, river flooding and ocean tides. According to the writings on clay tablets, a simple form of water clock was found to exist in ancient Babylon and Egypt. The concept of time, however, might be as old as human history. Events that we experience in life, such as changes of four seasons, the appearance of a full or a crescent moon, the rise and setting of our sun, the rise and ebb of tide, the blooming and withering of flower have been the subjects in literature, painting and music composition for generations. For several thousand years, people live at an ease pace in harmony with natural clocks. Only after the industrial revolution in the 18^{th} century, the pace of our daily life has become so fast, and now every minute and second counts. With the evolution from a mechanic clock to atomic clock in 1949 with an accuracy of one pear per 10^9 using an atomic resonance frequency of cesium-133, and more recently based on absorption spectroscopy of supercooled atoms in cesium fountains, accuracy of one part per 10^{15} can be achieved. Therefore, in the tiny atomic world every femtosecond counts!

With the invention of maser at 1954 and laser in 1959, nanosecond pulsed laser in 1960s, picosecond laser in 1970s and femtosecond laser in 1980s, scientists are equipped with powerful tools to investigate faster and faster processes in physics, chemistry and biology. Reaching a femtosecond time resolution, i.e., 10^{-15} s, is a very important milestone for science. It represents the time scale to characterize atomic motion in a potential well such as vibrations, in association or dissociation due to chemical reactions, and in atomic rearrangement due to conformation changes. Using a pump-probe approach with a femtosecond laser, laser-induced dynamics or chemical reactions can then be investigated via indirect spectroscopic means, with the help of theoretical modeling one could extract useful parameters and obtain physical insights to the processes.

Obtaining directly a picture of atomic movement in a femtosecond time frame, just like seeing atom's action in a movie, is the ultimate goal of time-resolved microscopy. However, human cannot see minute atoms by naked eyes or even by an optical microscope which has a spatial resolution about microns as limited by the wavelength of the visible light. In order to achieve atomic resolution of angstrom (10^{-9} m or 0.1 nm) one needs to use very short wavelength light. With short X-ray pulses such as generated by synchrotron radiation, one can "see" atoms in action. Another approach is to use an electron microscope. Due to matter-wave duality, electrons behave like light waves and can diffract. At energy of 200 KeV for an electron microscope, one can reach angstrom spatial resolution. At such a resolution, each individual atom on a flat sample can be seen clearly. However, the conventional electron microscope is designed

to run on a continuous mode, i.e., the electrons ejected out of the cathode are generated from a thermally heated electrode. The arrival of electrons at the sample plate follows a Poisson distribution and the sample image is a time-averaged picture with no time resolution. Although atomic resolution can also be achieved using atomic force microscope, scanning electron microscope and tunneling electron microscope, these techniques do not provide good time resolution. The viable solution to achieve time resolution is to apply a train of femtosecond laser pulses to the cathode to generate very short pulses of electrons. Such a modification can be done by modifying the conventional continuous-wave electron microscope, such as 1) properly choosing the composition materials for the electron gun; 2) installing mirrors inside the electron gun chamber and 3) adding windows for the laser pulses to get in from outside. The same femtosecond laser equipment can be employed with the laser beam split into two paths, one optical path as a pump pulse to initiate the structural changes, and the second path for laser pulse to be tripled in frequency and directed via mirrors onto the electrode. The generated short pulse of photoelectrons is used as a probing pulse. The time interval between the pump and probe pulses is varied and controlled by an electronically controlled delay stage as in the stroboscope technique. The repetition rate of the laser pulses is properly chosen, depending on the relaxation time for the perturbed system to return to equilibrium.

As a senior research scientist in collaborator with Prof. A. H. Zewail and Prof. R. A. Marcus at California Institute of Technology, I have worked on blinking of quantum dots and single protein molecules, laser-induced heat transfer, mobility of electrons and electron-phonon interactions in nano-structured systems (Fig. 1) such as gold, aluminum, silicon and GaAs. As the trend of IC industry, more and more transistors are packed inside a tiny chip to increase capacity and speed, heat dissipation of the small devices becomes an important issue. Understanding of nano-scale heat transfer is also important for laser applications in laser melting, ablation, deposition and microsurgery.

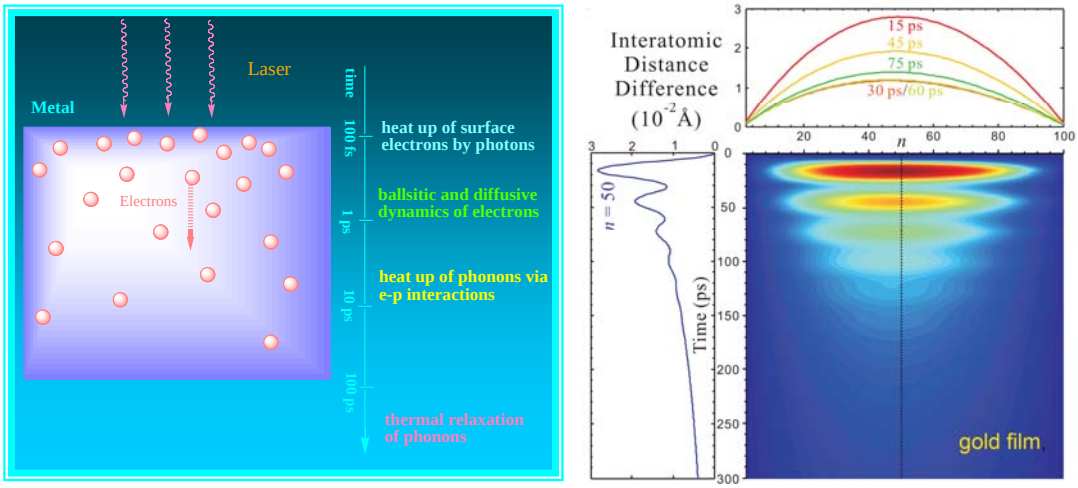

Figure 1. (Left) Schematic diagram for relevant physical processes and their time scale in laser-heating of a metal film. (Right) Spatial distribution (atomic site index n) and temporal behavior (time, ps) for the inter-atomic spacing changes of a laser-heat gold film, exhibiting rapid expansion and contraction.

In addition to studies of these materials, I also studied optically-induced phase transition of vanadium oxide using time-resolved electron microscopy/diffraction. Due to grain size distribution and heterogeneity of the sample, upon irradiation of a very short light pulse, some polycrystalline grains of the insulator phase are transformed into conductor phase, exhibiting phase transition from monolithic to tetragonal phases. By probing the position of the Laue diffraction rings (Fig. 2) and their time evolution, we have investigated the mobility and relaxation of hot charge carriers by watching the dynamic changes of phase transition in 4D.

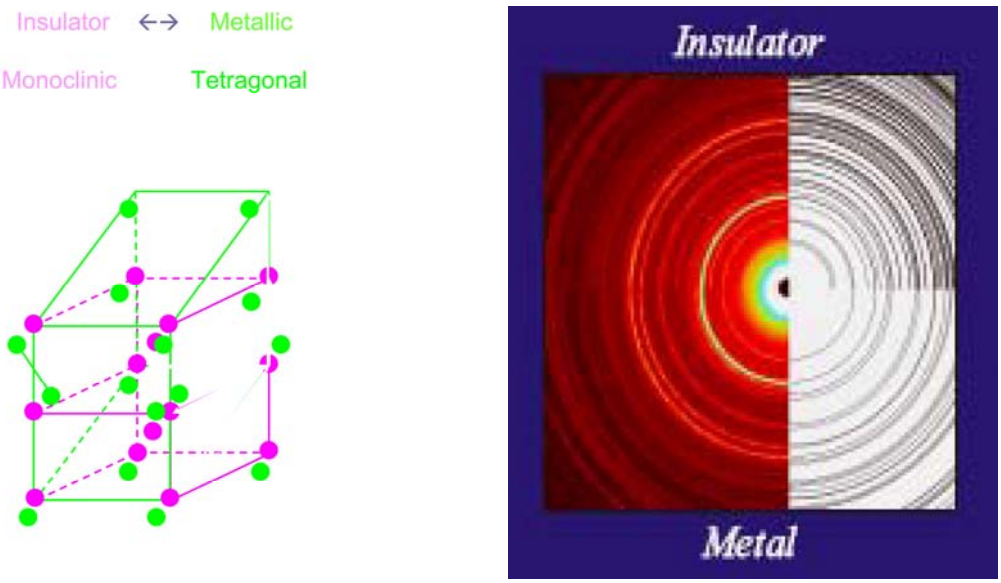

Figure 2. (Top) The crystal structure and symmetry of VO_2 in the insulator and conductor phases. (Bottom) The observed (red) and the simulated (black) Laue diffraction patterns showing differences between the insulator phase (upper half) and the metal phase (lower half).

Such an electron microscope in continuous mode allows one to obtain time-averaged, image of samples with atomic resolution as a conventional electron microscope. In pulsed mode, one can obtain structural changes as a video with a picosecond time frame or shorter. Although in this report we have only illustrated two examples, such as nano-scaled heat transfer and dynamic phase transition, by probing the atomic movement in high-T_c superconductors [3] one could shed light about the roles of conduction electrons, optical and acoustic phonons and the cooperative dynamics in superconductors. Time-resolved electron microscopy is still at its infancy, however, it is a multi-purpose and potentially very powerful technique. As compared to time-resolved X-ray diffraction which requires huge synchrotron machinery, this operation requires a smaller space as a conventional electron microscope plus an optical table for a pulsed laser and some small

optical devices. In addition, the scattering cross section of an electron is six orders of magnitude larger than that of an X-ray photon, therefore, electron diffraction is suitable for interfacial studies, nanocrystals, self-assembled monolayers, and small membrane crystals for which a large crystal is difficult to grow. The multitude of the applications in physical biology such as molecular recognition, hydration, charge transport, conformation changes and photosynthesis remains to be explored and certainly will bring fruitful results to many disciplines in sciences.

[1] J. Tang *et al*. J. Phys. Chem. **111**, 8957 (2007).

[2] V. A. Lobastov *et al*. Nano Lett. (in press, 2007).

[3] N. Gedik *et al.* Science, **316**, 425 (2007).