doi:10.1017/S143192762001702X
Microsc. Microanal. 26 (Suppl 2), 2020

Femtosecond TEM: Imaging Nanoscale Materials Dynamics at Temporal Extremes

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Stroboscopic time-resolved TEM capable of reaching temporal resolutions that go beyond detector limits has been in use for decades (see, for example, [1]). With few exceptions, this early work, and the more recent work focused on studying materials processes that form new structures or states without returning to the initial conditions on typical experimental timescales [2], probed mainly nanosecond dynamics. Again with few exceptions, the emphasis on going beyond nanoseconds to the sub-picosecond regime in the TEM began in earnest relatively recently with developments employing femtosecond (fs) pulsed lasers and commercial conventional instruments, principles of ultrafast pump-and-probe spectroscopy and scattering, and general concepts of stroboscopic imaging [3,4]. Though a variety of source types are now in use [5-7], the basic approach to reaching sub-picosecond (*i.e.*, hundreds of femtoseconds) time resolution in what is called ultrafast electron microscopy (UEM) is generally the same. In short, this involves limiting the number of electrons in each packet in order to preserve coherence and thus reach high spatial and temporal resolutions. Accordingly, this approach requires repeated pump-and-probe cycles at a fixed time point in order to accumulate signal, thus necessitating specimen relaxation to the pre pump-pulse condition before arrival of the next excitation pulse. While seemingly complex, numerous novel studies have been successfully conducted in this way [8-10], and the approach is now reaching a level of establishment that makes reflection upon current state-of-the-art capabilities as well as speculation on future advances timely.

Here, the goal is twofold: to provide an overview of the current state-of-the-art in stroboscopic fs TEM, supplemented with select recent examples, and to also provide an assessment of challenges yet to be overcome and the approaches currently being pursued to advance UEM spatiotemporal resolutions and to expand the application space for femtosecond-picosecond studies. Following a basic description of stroboscopic fs TEM operating principles and hardware, two recent studies of the direct imaging of photoexcited coherent acoustic phonons in metallic nanocrystals (plasmonic Au nanorods) and layered semiconducting materials (MoS_2) will be described [11,12]. Imaging of novel behaviors will be emphasized, including nanoscale anisotropic phonon dynamics and energy transfer and sequential excitation of lattice oscillations nucleated at individual defect structures, in addition to sensitivities to variations in dynamics driven by step-edges that are one unit-cell in height. Focus will then turn to discussing the current extremes of combined UEM spatiotemporal resolutions, with emphasis placed on understanding the interwoven nature of practical instrument parameters and fundamental physical phenomena. This will serve to define limits of interest to the imaging of ultrafast materials and chemical phenomena before ending with a discussion of cutting-edge technological developments currently taking place, with the goal of these efforts being to overcome the significant challenges that remain (see, for example, [13-15]). Thus, both the advances that have been made, as well as the opportunities that remain, will be placed into current context [16].

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[16] This material is based upon work supported by the National Science Foundation under Grant No. DMR-1654318. This work was supported partially by the National Science Foundation through the University of Minnesota MRSEC under Award Number DMR-1420013. Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research.