Chapter 1

Introduction[†]

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Being able to see the three-dimensional (3D) structure of a molecule or a condensed matter at the atomic level is crucial to our understanding of the substance and even its further applications. A perfect example would be the celebrated double-helical structure of DNA. Its discovery in 1953 (1, 2) had a huge impact on biology and medicine, and marked a new era in our understanding about life. Nowadays, when we talk about the biological activities and functions that occur in a cell, we speak in a way as if the biological macromolecules were visible in front of our eyes. Without clear knowledge of the molecular structures, scientific research endeavors would certainly be limited; the depth of our studies and the insights and applications derived from them could hardly reach their full capacities. For inorganic materials, too, without knowledge of the atomic arrangement in a unit cell, full understanding and even manipulation of the materials properties may not be achieved. In fact, the importance and impact of visualizing 3D structures at the atomic level were many times acknowledged by awarding the discoverers with Nobel prizes. A few examples include the development in solving the structures of inorganic salts, acknowledged in 1914 and 1915, DNA and hemoglobin (3) in 1962, borane (4) in 1976, photosynthetic reaction center (5) in 1988, ATP synthase (6) in 1997, and potassium ion channels in cell membranes (7) in 2003.

On the basis of the molecular or crystal structure, the research that can be pursued is outlined as follows. Static studies involve knowledge of the physical properties such as mechanical and thermodynamic properties, chemical stability, major forces that exist, etc.; theoretical modeling and calculations are made to further investigate the substance. Dynamics studies often put an emphasis on visualization of dynamical behaviors such as atomic motions, structural changes on different time scales, and reaction pathways. The combination of all these pieces of information allows us to know further the functions of

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Fig. 1. Several objects and their length scales.

the molecule or material, and to seek the possibilities of modifications and practical applications. Thus, studying structures at the atomic level has been one of the major research directions.

One important issue involved in the structure determination is the length scale (Fig. 1). Objects that can be seen by naked eyes are above tens of micrometers. With the use of an optical microscope, smaller objects with a dimension longer than the wavelength of visible light can be observed. However, below this length scale, visible light does not have the resolution due to the intrinsic diffraction limit. Atoms and molecules are much smaller, on the nanometer-to-angstrom scale. Therefore, one way to resolve this length-scale issue is to use light with a matching wavelength, which is in the range of x-ray, or small particles that also exhibit wave property due to the quantum effect, to detect molecular structures. As an example, for the studies presented in the following chapters, electrons are used and their acceleration by an electric field of 30 kV yields a wavelength of \sim 0.07 Å, which is much shorter than typical bond lengths and,

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Fig. 2. Sequence of a race horse galloping captured with the use of high-speed photography by Eadweard Muybridge (right). Without a proper temporal resolution, the observation would be similar to the combined image illustrated on the left.



Fig. 3. Examples of physical, chemical and biological processes and their time scales (adapted from Ref. 8). Femtosecond techniques provide the atomic resolution in time.

hence, provides the spatial resolution.

Besides the length-scale issue, traditional experiments suffer from one major problem, which is the poor temporal resolution. Without a proper temporal resolution, only the average atomic positions may be obtained, since atoms are constantly moving due to the zero-point and thermal energies. If important motions are much faster than the resolution of the experimental techniques, the observation cannot provide detailed information about the structure and dynamics involved. In photography, an analogy is shown in the left panel of Fig. 2. The equipment of an ideal temporal resolution [e.g., high-speed photography for capturing the sequence of a race horse galloping (Fig. 2, right)] allows the studies of the structure and dynamics at different moments, which may offer further understanding of the functions and the overall physical picture.

As illustrated in Fig. 3, the fundamental motions at the atomic level, such as electronic changes, vibrational and rotational motions, are in the femtosecond to nanosecond range. The important physical, chemical and biological processes on such a time scale are, for example, collisions, vibrational relaxation, proton transfer and chemical reactions, protein motions and light-induced transformations. To resolve these processes and probe the transient states, experimental techniques that have a suitable temporal resolution are required. For the last 20 to 30 years, such scientific endeavors were in the realm of femtophysics, chemistry and biology (δ , ϑ). The observables were typically measured by spectroscopic methods, for example, absorption and luminescence, reflectivity and transmission, mass or photoelectron spectra. While such measurements are giving important dynamics information, the results typically do not reveal the direct snapshots of the structure involved (10). In contrast, experimental techniques that can directly provide structural information with an ultrashort (femtosecond to nanosecond)

temporal resolution have clear advantages for studies of transient structures.

For the reasons given above, time-resolved x-ray and electron diffraction methods have been under development for more than two decades. A review of their progress until 1997 can be found in Ref. 10. Ultrashort x-ray pulses with a sub-picosecond temporal width were successfully produced in 1996 (11); generated by another method, the pulses were used on a real material and diffraction changes were observed in 1997 (12). Various groups reported ultrafast x-ray diffraction studies in 1999 and, interestingly, most of them were made on semiconducting materials (13-15). Since then, this technique has been applied to the studies of nonthermal melting (16), inertial dynamics of thermal disorder (17), dynamics of optical (18) and acoustic (19-21) phonons, the motion of charges (22), solid-solid phase transitions (23), and transient structural changes (24) even in the solution phase (25, 26). A brief review that covers the work on transient crystalline structures can be found in Ref. 27.

In our laboratory, the methods of choice have been ultrafast electron diffraction and microscopy (28). The advantages of using electrons are many (29). First, the large scattering cross section due to the order-of-magnitude stronger electron-matter interaction (compared with the light-matter interaction) provides high sensitivity in detecting small changes and also surface sensitivity for interfacial studies. Second, electrons are less damaging to specimens per useful scattering event. Third, apparatus can be built on the tabletop scale, which allows us to avoid competing for the scarce resource such as a synchrotron x-ray facility. With the use of femtosecond laser pulses, the temporal width of electron pulses generated from a photocathode through the photoelectric effect can be as low as several hundred femtoseconds in the low-flux limit (30).

The apparatus of ultrafast electron crystallography (UEC) was the fourth system

of the time-resolved electron diffraction technique in our group, specifically dedicated to condensed-matter studies. The earlier three generations were chronologically developed for gas-phase research (31, 32). Unlike other groups that also implemented ultrafast electron diffraction for materials studies in transmission geometry at roughly a similar time (33, 34), our UEC system (35) can be operated in both reflection and transmission geometries for a wider range of applications. Furthermore, research focuses are quite different: for others, the strong emphasis is on irreversible ultrafast melting (33, 36, 37) or on coherent film motions and electronic Grüneisen parameters (38-40); for us, the experiments are conducted on reversible structural changes, and the research topics include (and are not limited to) nonequilibrium structural dynamics (41-44), phase transformations (45), highly correlated materials such as high-temperature superconductors (46, 47), interfacial thin films (48-50), and surface assemblies (51-53). Most of these topics will be covered in this thesis.

Chapter 2 describes the fundamental principles related to UEC studies and the dynamics information that may be obtained. Although electron crystallography has been developed into a complex subject, our experience shows that the geometrical consideration and the kinematic (elastic) scattering theory are capable of capturing most of the physical picture from the observed dynamical changes. The UEC methodology, apparatus, and discussion of several experimental concerns are given in Ch. 3.

Chapters 4 and 5 present the studies of nanometer-scale structures of semiconducting materials. In Ch. 4, gallium arsenide is the prototype system and its detailed study forms the foundation for the application of UEC to various other systems (42). Following the ultrafast heating made by femtosecond light pulses, we observe a universal behavior of diffraction changes, with amplitudes far exceeding those of thermal

heating (in a time of ~ 10 ps); the lattice change can be monitored with an accuracy of ~ 0.001 Å. The physical picture for such structural dynamics is described with emphasis on the motion of atoms under the influence of optical and acoustic vibrations, the potential anisotropy of the lattice that results in the weakening of bonding, and the diffusion at much longer times. This work is the result of collaboration with Dr. Nuh Gedik who initiated the idea of working on a quantum-well structure for both reflection and transmission studies.

In Ch. 5, the same picture is applicable to the structural dynamics of zinc oxide nanowires, whose colossal expansion, as a result of the induced antibonding character, is highly anisotropic (quasi-1D) and two orders of magnitude higher than that expected at thermal equilibrium (44). This unanticipated ultrafast carrier-driven expansion highlights the optoelectronic consequences of nanometer-scale morphologies. Observation of the electron refraction phenomenon is also discussed. This work is the result of collaboration with Dr. Changshi Lao who contributed the idea of studying nanostructured materials. Prof. Zhong Lin Wang at Georgia Institute of Technology kindly provided the specimens.

Chapters 6 to 8 describe the UEC studies of several highly correlated materials, including vanadium dioxide and high-temperature superconducting cuprates. In Ch. 6, we report the visualization of transitional structures from the initial monoclinic to the final tetragonal phase in crystalline vanadium dioxide (*45*); the change is initiated by near-infrared excitation. By studying the spatiotemporal behavior from all observed Bragg diffractions in 3D, the femtosecond primary vanadium–vanadium bond dilation, the displacements of atoms in picoseconds, and the sound wave shear motion on hundreds of picoseconds are resolved, which elucidates the nature of the structural pathways and the nonconcerted mechanism of the solid-solid phase transformation. This

work is made possible because Prof. Liu Hao Tjeng generously gave us some crystals, Prof. George R. Rossman provided the crystal-cutting equipment, and Prof. Nai-Chang Yeh allowed me to use the pulsed laser deposition system for the making of thin films; Dr. Peter Baum is the collaborator of this work. I have to admit that we were fortunate because the plan of cutting and polishing the last crystal did work, and the last product during the many trials of thin-film making gave the correct phase and good crystallinity.

In Ch. 7, an unanticipated nonequilibrium phase transition in lanthanum cuprate is reported, which is recognized through the observation of "structural isosbestic" points in the temporal evolution of diffractions (46). Time scales of the structural dynamics of such a transition are examined, and the observed transient behavior also displays a threshold effect for the dependence of c-axis expansion on the excitation laser fluence. This threshold for photon doping occurs at ~0.12 photons per copper site, which is intriguingly close to the density (per site) of chemically doped carriers needed to induce superconductivity. The specimens for this work are provided by Drs. Ivan Bozovic and Gennady Logvenov at Brookhaven National Laboratory, and Dr. Nuh Gedik is the collaborator. The finding of structural isosbestic points also assists the understanding of other systems that exhibit similar diffraction changes in time.

In Ch. 8, we provide direct evidence of the role of structural dynamics for electron pairing in high-temperature superconductors; selective atomic motions (buckling of copper–oxygen planes) participate in the anisotropic electron–lattice coupling (47). Following carrier excitation by polarized femtosecond heating pulses, the transient structures are examined for different dopings and temperatures. The deformation amplitude reaches 0.5% of the *c*-axis value of 30 Å when the light polarization is in the direction of the copper–oxygen bond, but its decay slows down at 45°. These findings

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suggest a selective dynamical lattice involvement, with the anisotropic electron-phonon coupling being on a time scale (1 to 3.5 ps depending on the direction) of the same order of magnitude as that of the spin exchange of electron pairing in the high-temperature superconducting phase. The specimens for this work were synthesized and characterized by Dr. Enrico Giannini. Dr. Fabrizio Carbone is the collaborator and an expert in the field of high-temperature superconductors. It was fortunate that during the time of working with him, my suggestion about the polarization-dependent experiments made contribution and helped solidify the conclusions.

Chapters 9 to 11 report the application of UEC to the studies of interfacial water assemblies and self-assembled monolayers on substrates. In Ch. 9, the structure of interfacial water assembly on highly oriented pyrolytic graphite, a hydrophobic surface, is determined to be ordered in the vertical direction, contrary to the expectation that the strong hydrogen bonding of water on hydrophobic surfaces would dominate with suppressed interfacial order (*53*). Because of its terrace morphology, graphite plays the role of a template. Dynamically, following the excitation of graphite by an ultrafast infrared pulse, the interfacial ice structure undergoes nonequilibrium phase transformation, which is identified in the hydrogen-bond network through the observation of a structural isosbestic point.

In Ch. 10, the full account of the structure and dynamics of interfacial water assembly on hydrogen-terminated silicon(111), another hydrophobic surface, is provided. Structurally, due to the lack of guiding forces from the substrate surface and morphology, the ice assembly is polycrystalline with randomly oriented crystallites being of the cubic form, ice *Ic*. Crystallites with {110} preferred orientation are found to be close to the ice-vacuum interface, which may have its origin from the viewpoint of energetics.

Dynamically, upon the ultrafast heating of the substrate, the interfacial ice structure undergoes four stages of changes—ultrafast melting, nonequilibrium phase transformation, annealing, and restructuring—that are closely correlated with the substrate dynamics. Once again, the phase transformation is identified through the observation of structural isosbestic points, and the lattice expansion of ice is found isotropic. We discuss the time scales involved, the nature of energy transfer between the substrate and interfacial ice, and, from the peculiar evolution of structural dynamics observed, its implications and our suggestion for future theoretical investigations. Dr. Nuh Gedik is the collaborator of this work.

In Ch. 11, the first study of self-assembled adsorbates on metal surfaces by UEC is reported (*52*). We investigate single-crystal clean surfaces of Au(111) with and without a monolayer assembly of 2-mercaptoacetic acid as a result of the reaction from 2,2'-dithiodiacetic acid. In addition, a monolayer of iron hemes is studied. Structural dynamics of the substrate (gold) and adsorbate(s) following an ultrafast temperature jump can be observed and isolated. The phenomenon of ultrafast annealing, i.e., an increased order in the originally random assembly observed only on an ultrashort time scale, is recognized, which also has influence on the substrate dynamics. This work is the result of collaboration with Dr. Chong-Yu Ruan.

Lastly, Ch. 12 describes a systematic theoretical study of structural dynamics for a substrate and an adsorbate, and makes comparison with experimental results (*54*). With the use of the harmonic lattice model of a chain of atoms, including anharmonic forces, influences of the impulsive force on the temporal behavior of Bragg diffraction are investigated, and the roles of damping and anharmonicity are also discussed. Extensive simulations are made in order to gain an understanding of the controlling factors of the

atomic motions in the substrate, with or without the adsorbate. The results elucidate the importance of coherent wave propagation in the nonequilibrium regime and provide the atomic-scale description of surface and bulk dynamics. The influence of the attenuation length of the impulsive force and the thickness of the substrate (adsorbate) are also considered. For adsorbates, the mismatch of force constants and the coupling with the substrate are examined, thus establishing the conditions for wave-type propagation. Dr. Jau Tang initiated this project of theoretical investigation, and I am grateful that I had the opportunity to participate in it.

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