Chapter 1

Introductory Chapter: Electron Microscopy - Research Highlights

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http://dx.doi.org/10.5772/intechopen.80729

1. Introduction

Scientific knowledge begins with observation. Scientists use observation to obtain data and verify theories and hypotheses. The most straightforward method of observation consists in imaging an object under study. Therefore, microscopy is an integral part of modern research in natural sciences. Here, I highlight recent innovations of transmission electron microscopy such as the development of new techniques of sample preparation, application of electron diffraction to study atomic displacements in disordered materials, determination of local structural variations in glassy materials, and imaging dopants atoms in quantum dots. The highlights may interest researchers working on nanoscale phenomena in solid state physics, technology, materials physics, and engineering.

2. A novel method of sample preparation for transmission electron microscopy

Improved instrumentation and optics significantly contributed to the development of transmission electron microscopy (TEM) with considerable effort put into innovative techniques for preparation of samples and introduction of new equipment, which progressed from the ion-beam polishers to tripod polishing and focused-ion-beam systems. Even though the latter can damage a specimen, the method is almost universally used for the sample preparation in electron microscopy. To prevent sputtering damage, a photoresist or a combination of a photoresist and an inorganic film may be used.

The sample geometry for TEM analysis in a majority of studies is the thin-foil. A new technique of sample preparation has been developed to enable transmission microscopy in most basic equipment with the use of usual imaging modes [1]. As an example of TEM by specimen design, the strain in thin film planar devices has been studied. The strain is one of the important parameters for understanding nanoscale phenomena in physics because it controls the mechanical and electronic properties of materials. The new measurement technique of electron microscopy proposes an original design of the specimen geometry to apply the technique in basic conventional TEM, *i.e*. by exploiting the moiré imaging phenomenon. The Moiré patterns are analyzed for the strain, the lattice parameters, orientation, and distortions. A new method of two-sample preparation is proposed to utilize the properties of moiré patterns and improve the spatial resolution of strain maps. The method explores cutting a thin lamella sample into two pieces to provide precise control of parallelism of the two superimposed surfaces. The misorientation of the two surfaces is only 0.05° that is smaller by one order of magnitude than typical Bragg angles in the range of 0.3–0.6° and the zone, which needs to be imaged, is orientated almost in the same direction as the reference lattice. The spatial resolution of TEM imaging obtained by applying this sample preparation procedure is about one nanometer that is achieved by controlling rotations of the samples during preparation.

3. Disordered materials studied by electron transmission microscopy

The atoms vibrate in the matter at room temperature. The effect of vibrations is observable from diffraction patterns of electron microscopy. Vibrating atoms introduce a diffuse background of low intensity superimposed with the diffraction peaks. Without the thermal diffuse scattering (TDS) diffraction angles of stationary atoms would give a set of discrete lines. Electrons, as well as x-rays and neutrons, are characterized by a wavelength, which is dependent on an accelerating voltage applied between the cathode and the anode. A typical wavelength of an electron in a TEM instrument is 0.04–0.02 Å, *i.e.* by a few orders of magnitude smaller than the wavelength of x-rays. Therefore, much smaller Bragg angles can be achieved that enables crystalline order to be studied with higher precision. Also, x-ray analysis requires rotation of a sample, whereas electron diffraction does not. A range of disordered lattices can be studied by using electron transmission microscopy – flexible framework structures, disordered solid solutions, stacking fault structures, and materials susceptible to structural instabilities such as novel perovskite metal-halide semiconductors.

Diffuse scattering has been studied in the molecular crystals, which experience large molecular displacements as a result of thermal molecular vibrations [2]. The dynamic disorder in molecular systems contributes to fluctuations of the transfer integrals, *i.e*. to charge carrier transport in disordered molecular solids and the energy distribution of transport sites. The lattice vibrational modes of a range of organic semiconductors have been studied from electron diffraction patterns in TEM. The research illuminates the interrelation of thermal lattice fluctuations and molecular structure of organic semiconductors.

4. Spatial heterogeneity in metallic glasses studied by high-angle annular dark field microscopy

Glasses have been considered as liquids frozen by quenching of high-temperature melts. Metal glasses are hard to prepare because compared to organic materials and silicates metals readily crystallize during solidification that introduces heterogeneities in the amorphous materials structure. The heterogeneous nature of metal glasses has long escaped an experimental evidence since nanoscale crystal-like aggregates in amorphous solids appear at a very short length scale, which is not detectable by high-resolution electron diffraction methods.

To reveal crystal-like aggregates at nano-scale and study the local atomic structure of spatial heterogeneous metallic glasses, researchers use advanced experimental methods of angstrom-beam electron diffraction (ABED) and aberration-corrected scanning transmission electron microscopy (STEM) [3]. The crystalline phase is detected by the technique of high-angle annular dark field (HAADF) imaging in STEM. In HAADF, the scattering angles are large and incoherent thermal diffuse scattering surpasses the coherent Bragg scattering. Being sensitive to the atomic numbers, HAADF provides contrast images of compositional non-uniformities in materials. The structurally different regions in the metallic glass are observed as dark and bright areas in HAADF STEM images and analyzed by using ABED to detect the local atomic configurations. The structural variations within the glassy material result in spatial heterogeneity of metallic glasses that manifest itself in a fluctuation of density occurring without fluctuation of chemical composition. The structural heterogeneity has important implications in glass science and technology because many of the material properties such as the glass-forming ability and the elastic behavior are structurally dependent.

5. Ultra-thin graphene oxide support film for TEM observations of core-shell nanocrystals

Over the last five decades, SiO_2 has been intensively studied as the basic ingredient in field-effect transistors, silicon photovoltaics, and nanoscale light-emitting sources. Metal-oxide-semiconductor technology is dominating for very large scale integration applications, enabling smaller dimensions, a faster switching speed, and a lower power dissipation. Ability to control the oxide thickness with an angstrom precision facilitates the fabrication of ultra-small devices operating at a higher drive current. Despite the successful implementation of planar SiO_2/Si nanostructures in transistors, the device application of Si nanocrystals in electronic and optoelectronic devices is still hindered due to low carrier concentration and low charge carrier mobility. Although the optical and electronic properties of silicon nanostructures are remarkably dependent on the modification of the defect ensemble at the Si nanocrystal-SiO_2 interface, direct imaging of the amorphous structure surrounding silicon nanocrystals has been found difficult due to the insufficient contrast of electron microscopy. The use of atomically thin graphene oxide supports in electron microscopy of colloidal silicon quantum dots reveals the amorphous structure of the surrounding core with the core

thickness being affected by the concentration of doping atoms [4]. The insufficient doping might stem from the aggregation of the dopant and the silicon atoms in a partially oxidized amorphous shell, which forms on the top of a crystalline silicon core.

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