CHEM 681 Seminar

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Room 2104, 4:00 p.m.

High Resolution Transmission Electron Microscopy: theories and applications

In materials science, people are always interested in viewing the microscopic structure of a solid at atomic resolution, because it is the microscopic structure of a solid that controls most of its mechanical, electrical, chemical, and thermal properties. Among the experimental techniques that achieve atomic resolution, high-resolution transmission electron microscopy (HRTEM) is the ideal—indeed the only—tool to image not only the morphology of solid surface, but also its interior structure. The resolution of HRTEM imaging presently approaches 1 Å. The reliability of determining the position of atom columns at crystal defects has even reached 0.01 Å. This development makes an important transition of TEM technology: from formerly qualitative one to quantitative one. This enables us to study the complicated and artificial structures, crystal defects, precipitates, superlattice, interfaces and so forth, down to the atomic level easily.

Figure 1 shows the ray paths and the image formation in a modern HRTEM. The electron beam is produced in an electron gun , then focused by a series of condenser lenses to produce the incident beam at the specimen with the desired diameter (10 nm or 10 um) and convergence (10^{-2} to 10^{-5} radians) (not shown in fig.1). The specimen transmits this planar electron wave, interacts with it, and the resulting electron wave $\psi_e(x,y)$ at the exit plane of the specimen carries information about the atom arrangement in the specimen $\psi_e(x,y)$ is a complex function with an amplitude and a phase component.

The objective lens focuses image and series of intermediate and/or projector lens control the magnification of the final TEM image. The back focal plane of the objective lens contains the Fourier transform $\Psi(u,v) = F\psi_e(x,y)$ of the object, and the following lens system reconstructs the object function $\psi_e(x,y)$ in the image plane as $\psi(x,y)$ by inverse Fourier transform. For the perfect lenses $\psi(x,y) = \psi_e(x,y)$ and $\psi(x,y) = \psi_e(x,y) * t(x,y)$ for the real system where t(x,y) is the spread function due to the imperfections of the lens

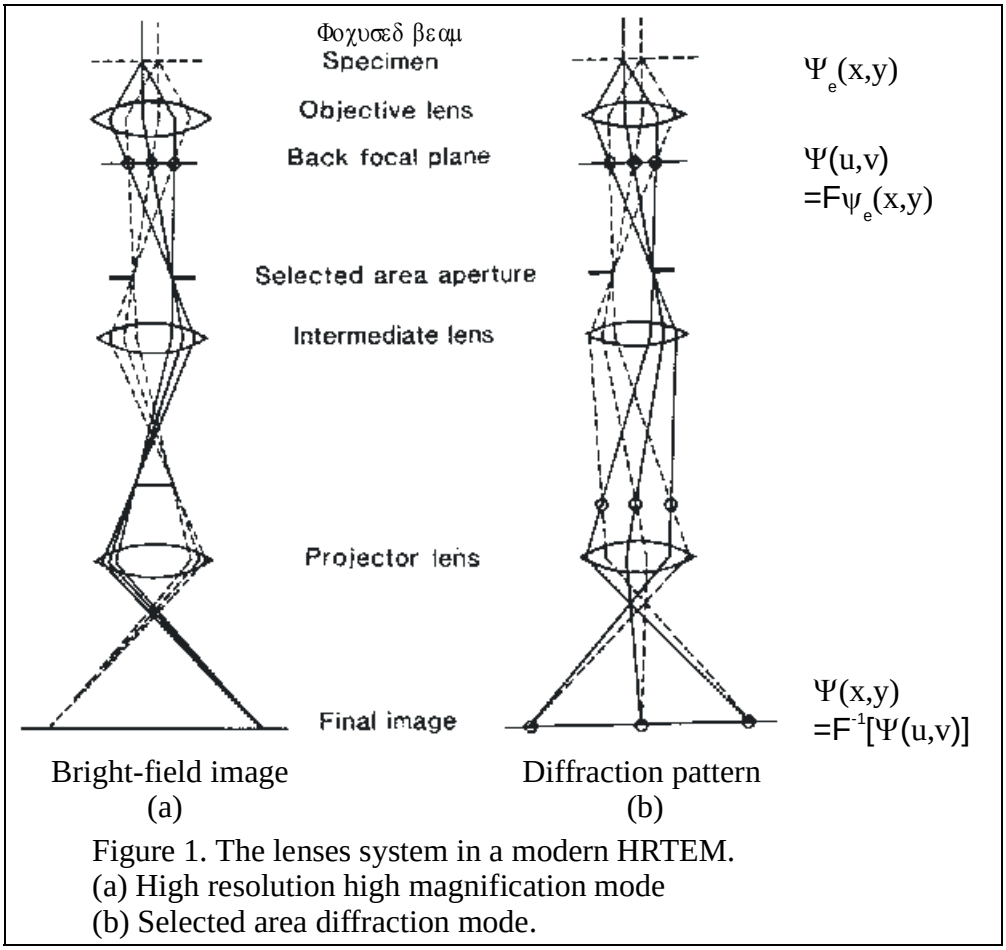

Figure 1. The lenses system in a modern HRTEM.
(a) High resolution high magnification mode
(b) Selected area diffraction mode.

action (aberrations and defocus). Among these three lenses system, the objective lens is the most important one. Because it is the first magnifying lens, any imperfections in the objective lens will be magnified by the other lenses and in most cases, the instrument resolution of TEM is controlled by the its defects.

Three kinds of contrasts-amplitude, diffraction, and phase contrast, which stem from the specimen-beam interactions such as absorption, diffraction, elastic scattering, and inelastic scattering (see Fig. 2), contribute to the formation of the TEM image.

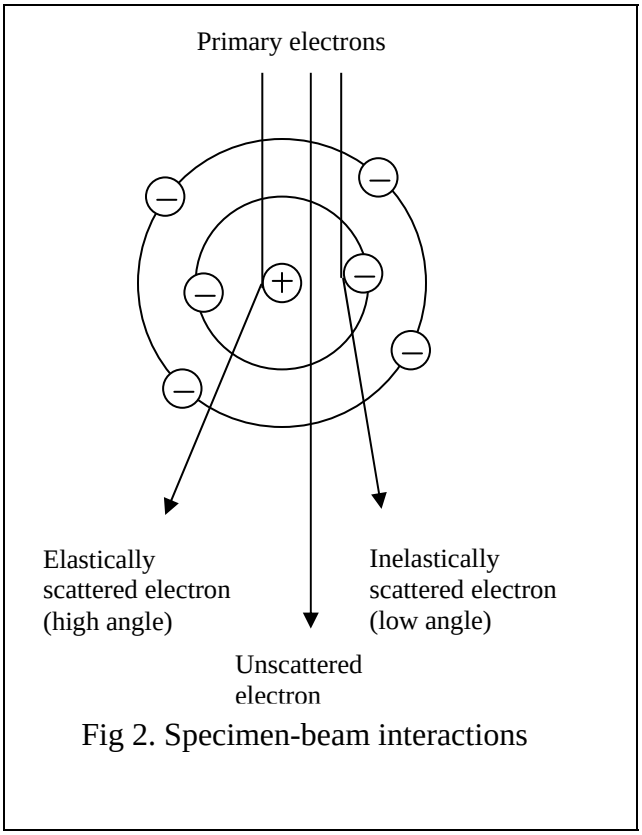

Fig 2. Specimen-beam interactions

Electrons may be absorbed into thick or heavily stained portions of the specimen or into areas of atoms with high atomic numbers. Because most of the electrons can pass through the specimen, the absorption by the specimen does not contribute significantly to image contrast. Elastically scattered electrons are those produced when electrons from the beam interact with the nuclei in atom from the specimen. These electrons undergo a large deviation in their path but little or no energy loss. Elastically scattered electrons contribute to both amplitude and diffraction contrast in an image. Inelastically scattered electrons are those produced when electrons from the beam interact with electrons in atoms from the specimen. These electrons are characterized by a loss of energy and only a slight deviation in their path. They contribute to the phase contrast. Usually the formation of image for amorphous specimen is du to the amplitude contrast, for crystalline specimen in preferred

orientations due to diffraction contrast, and for very thin and/or low atomic number specimen due to the phase contrast.

Improvement of the resolution to the atomic level is the impetus of the development of TEM. The resolution of the first TEM instrument, constructed in 1934 according to Ernst Ruska's design, just surpassed that of the light microscope (Ernst Ruska was awarded 1986 Noble Prize in Physics for his TEM design), but in the late 40's, the TEM resolution could reach 10 – 20 Å. The modern TEM can reach the resolution of about 2 Å and the best one is 1 Å. This resolution allows us to view the object structure at atomic level.

A clear definition of resolution is not easily given for a TEM, because a lot of factors, such as the electron beam, the object, the electron microscope itself, the detector can have effect on the instrument resolution. For thin objects, two kinds of resolution are used: point-to-point resolution (or structural resolution) and information limit, with the former used more often.

Point-to-point resolution means the finest detail that can be interpreted in term of the structure. This resolution is related to the wavelength λ of electron beam and the lens defects, such as the astigmatism, chromatic and spherical aberration. The spherical aberration is particularly important because there is no convenient way to correcting it. The maximum point-to-point resolution can be expressed by eq. 1:

$$\rho_s = 0.65 C_s^{1/4} \lambda^{3/4} \qquad (1)$$

where λ is the wavelength of the electron beam and Cs is the spherical aberration constant and is typically 1 or 2 mm for an objective lens. The information limit is

defined as the finest detail that can be resolved by the instrument, irrespective of a possible interpretation. The transfer function of the microscope cuts all the information beyond the information limit. For a thin specimen, this limit is mainly determined by the envelope of chromatic aberration (temporal incoherence) due to the wavelength spread of the electron beam. The information limit can be estimated as:

$$\rho_I = \left(\frac{\pi \lambda \Delta}{2} \right)^{1/2} \qquad (2)$$

where Δ is the half-width of Gaussian defocus spread due to chromatic aberration. Usually, the information limit is smaller than the point resolution.

As shown in eq. 1, the point resolution ρ_s is dependent on the wavelength (thus the voltage) and the sperical aberration constant Cs. One way to decrease ρ_s is to increase the accelerating voltage V. For example, if C_s = 1 mm the ρ_s is 0.2 nm for λ = 2.2 pm (V = 300 keV by using $\lambda = 1.226(V)^{-1/2}$ nm) and 0.12 nm for λ = 1.2 pm (1000 keV). However, besides the increased cost, the very high voltage might increase the radiation damage of the object, especially for light atoms such as in polymer or biological specimen.

Because Cs depends mainly on the pole piece dimension and the magnetic materials used, not much improvement can be expected. Hence, at present, the resolution of the Tem is limited by Cs. In the far future, the major improvement can be expected by using a system of quadrupole, hexapole, and/or octupole lenses, using superconducting lenses or microlenses.

Another promising approach of increasing the resolution of HRTEM voltages is to retrieve the complex-valued electron wave function, $\psi_e(x,y)$ at the exit plane of the object, directively from experimental images using 'off-axis electron holography' method or retrieve the electron wave function $\psi_e(x,y)$ from a series of HRTEM images recorded at different focus settings of the lens using 'focus variation method'. These methods may allow the TEM at intermediate voltages to reach an ultimate resolution of 0.1 nm.

Besides the structural analysis, HRTEM can be also used as composition analysis technique. Because the primary electrons will be inelastically scattered by the electrons of the atoms in the sample and thus loss energy and also x-rays will be produced when the primary electrons interact with the sample, the detectors for X-ray emission (energy-dispersive spectrioscopy (EDS) if the energy of the x-rays is measured) and electron energy loss spectroscopy (EELS) may be added to the TEM column. These attachments allow determination of the presence, amount, and distribution of the elements in the sample.

Because of the high resolution and viewing of the bulk structure, HRTEM has found applications in every branch of materials science, such as alloys, crystal defects, superconductors, minerals, carbon structures, cage structure, small particles or nanoclusters, catalysts, and polymers. Importantly, HRTEM has some unique advantages in several fields.

One of the greatest contributions of HRTEM to structure science has been the routine elucidation of the true structures of ultrafine metal or metal oxide particles (~ 100 Å). HRTEM can give not only the shape and size but also the structure information of these nanoparticles while other techniques always have problems to investigate the

structure of sub-100 Å particles. Another feature of HRTEM in applications is that it can view the isolated defects, such as stacking fault, dislocations, gain boundaries, in crystals. These high-energy defect sites frequently exert a controlling influence on the physical properties, catalysis or phase-transformations mechanisms of crystals. The TEM results play an very important role to help understand the behaviors of crystals in different environments.

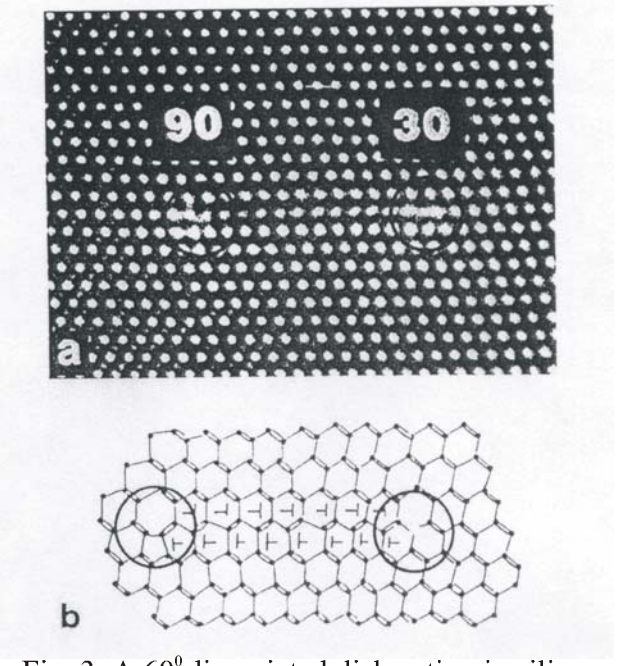

Fig. 3. A 60^0 dissociated dislocation in silicon a. Experimental image; b. Structural model.

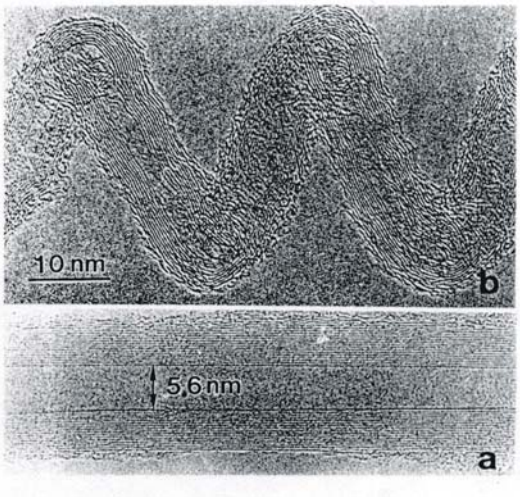

Fig. 4 HRTEM images of carbon nanotubes
a. Straight tube; b. Helix-shaped nanotubes.