Advances in high-resolution transmission electron microscopy for materials science

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Introduction

The most important benefit of high-resolution transmission electron microscopy (HRTEM) applied to problems in materials science is its ability to provide real-space images of the local structure of thin specimens at atomic resolution. This enables direct observation of the bulk structure of complex materials and also direct imaging of local structural variations at defects, interfaces, and surfaces. During the past 25 years significant advances have been made in the instrumentation available for HRTEM including new electron sources, aberration correctors, digital detectors and controlled sample environments. These have enabled improvements in spatial resolution and, although not discussed here, spectroscopic capability and sensitivity, allowing HRTEM to be used in a wider range of complex problems in materials science. In parallel, progress has also been made in improving the computational simulation and processing of HRTEM data. In this article we briefly review a selection of the major technological advances over the past 25 years which have enabled this progress.

Electron Sources

The widespread availability of field-emission electron sources for TEM/STEM instrumentation has been one of the most important advances in instrumentation in the past 25 years. For HRTEM, field-emission sources have provided an increase in image resolution and have promoted the development of computational techniques that further extend image resolution and image interpretability.

Cold field-emission guns (C-FEGs) have long been employed in dedicated scanning transmission electron microscopes operating under ultra high vacuum conditions, utilising the high brightness and low energy spread characteristic of these sources [1]. However, low total emission currents precluded their successful application to conventional TEM. In addition, the small isoplanatic patch formed from a C-FEG source proved problematic for the larger field of view required in HRTEM [2]. The Schottky field-emission source [2, 3] addressed these problems by providing a stable, high current output with a larger isoplanatic patch, in addition to requiring less stringent vacuum requirements, albeit at the expense of a larger energy spread and lower brightness. Intense development activity during the early 1990s saw the successful application of Schottky field-emission sources in conventional HRTEM instruments [2, 3]. Recently however, improved C-FEGs have been developed that provide high brightness, higher total current and less stringent vacuum requirements that are suitable for application for HRTEM [4]. One of the limiting factors in determining the information limit in HRTEM is the energy spread of the source and an alternative route to reducing the energy spread is to use monochromated electron sources which has now been realised experimentally with several different designs operating at intermediate voltage [5-7].

Monochromator geometries have been proposed and tested that can broadly be divided into those with straight optical axes (typically Wien filters) [5, 8, 9] and those with curved axes (typified by omega geometries) [6, 10]. The former require both electromagnetic and electrostatic elements in order to satisfy the Wien condition whereas the latter can be constructed from purely electromagnetic or electrostatic elements [5]. For any successful design the monochromator must provide sufficient current density for HRTEM at a given energy resolution, determined by the energy selecting slit width.

Prior to these developments in field-emission sources HRTEM instrumentation had relied on thermionic W or LaB6 electron sources [11]. FEG sources provide a much higher level of coherence with associated improvements in resolution defined by the information limit in the phase contrast transfer function (PCTF), beyond the point resolution. In contrast, the PCTF of a LaB6 instrument rapidly decays to zero beyond the point resolution, limiting the range of spatial frequencies transferred relative to those in an FEG instrument. However, the intrinsic positive spherical aberration of the objective lens leads to rapid oscillations in the PCTF beyond the point resolution, as shown in Figure 1. Thus, although high spatial frequencies are transferred into the real-space image, high-resolution data may not be directly interpretable in terms of atomic positions [12]. Finite spherical aberration also leads to delocalisation of high-resolution features as shown in Figure 2. This enhanced, but not directly interpretable information provided by FEGs initiated renewed theoretical and computational efforts. Exit wavefunction restoration using a focal series of images provides a solution to the problem of recovering spatial frequencies beyond the point resolution to close to the information limit of the microscope [13, 14]. Importantly, this indirect approach provides both phase and modulus of the exit-wavefunction for direct comparison with the structure of the object using simulated exit wavefunctions with only structure and specimen thickness as unknown variables.

Aberration Correctors

One of the long standing goals in electron optics has been the correction of the positive spherical aberration that is present in all round electromagnetic lenses [15]. The essential optical elements used in all practical correctors are non-round (multiply) lenses as originally proposed by Scherzer [16]. Designs for various correctors have been proposed (for reviews see [17, 18]). However,
In high-resolution electron microscopy (HRTEM), it is only relatively recently that these elements have been developed to a level where improvements to the highest performance uncorrected instruments can be made. For the most part this has been due to the extreme mechanical precision and electrical stability required in the corrector elements and the need for sophisticated computer control of the corrector alignment and aberration measurement. However, in the late 1990s significant improvements in resolution for both HRTEM and STEM were demonstrated, although in this article the latter geometry will not be considered further. We also note that correctors for both spherical and chromatic aberration have also been recently described based on a combination of electromagnetic and electrostatic multipole elements.

The most commonly available correctors for HRTEM are based on a pair of strong electromagnetic hexapole elements together with additional round lens doublets [22]. Correction is achieved due to the fact that the primary, non-rotationally symmetric second-order aberrations of the first hexapole (a strong three-fold astigmatism) are exactly compensated by the second hexapole element. Owing to their non-linear diffraction power, the two hexapoles induce a third-order spherical aberration which is rotationally symmetric [23] and proportional to the square of the hexapole strength. This aberration has a negative sign, thus cancelling the positive spherical aberration of the objective lens. For HRTEM applications it is essential that the corrector is aplanatic to provide a sufficiently large field of view which is achieved by matching the coma-free plane of the objective lens to that of the corrector using a round transfer-lens doublet. To reduce the azimuthal (anisotropic) component of the off-axial coma the current direction of the first transfer-lens doublet is opposite to that in the objective lens.

In addition to these primary optical elements, commercial correctors [19, 24] contain a number of additional multipole elements for alignment and correction of any residual parasitic aberrations. The main difficulties associated with the practical operation of these complex electron optical components are the requirements for sophisticated computer control of the various elements and a systematic alignment procedure providing rapid, accurate measurement of the aberrations. In practice, this is achieved using measurements of the two-fold astigmatism, and defocus, from a tableau of diffractograms recorded at known beam tilts (Figure 4).

These measured values are subsequently used to calculate the aberrations present and the appropriate currents to the optical elements are then applied under computer control. The optimisation of imaging conditions for corrected instruments and the interpretation of the images obtained has also required renewed analysis.

If the spherical aberration of the objective lens is exactly corrected and the defocus is also set to zero then the phase contrast transfer function equals zero for all spatial frequencies up to the information limit set by partial coherence while the amplitude-contrast transfer function is unity.

Under these conditions HRTEM can be carried out under pure amplitude contrast conditions in a mode which is not available in a standard uncorrected TEM [28]. Conventional phase contrast HRTEM images can be obtained using several optimal conditions in which the spherical aberration and defocus are balanced against either the fifth order spherical aberration $C_5$ or the chromatic aberration coefficient $C_7$ [26].
In-Situ HRTEM

In HRTEM studies the influence of the electron beam and high-vacuum environment must be considered when designing experiments and analysing their results. Typical high vacuum, room temperature environments are frequently far removed from the typical operating conditions for many materials. The development of high precision engineering that extends the functionality of HRTEM instruments to provide a range of controllable specimen environments has enabled studies of the dynamic atomic-scale structure of materials under realistic operating conditions. In-situ and environmental HRTEM also benefits from the other advances discussed in this article; field-emission sources, electron optical aberration correction and improved detector technology.

In-situ TEM began in the 1970s with the use of modified high-voltage microscopes that enabled the observation of relatively thick samples under a range of conditions using early heating, staining and gas reaction stages [27]. Major advances in the 1980s and 90s in medium and low-voltage HRTEMs led to a re-examination of technologies for in-situ HRTEM and its potential applications [28]. To record useful HRTEM images requires that scattering of the primary electrons is dominated by interactions with the specimen, rather than by the gas molecules of the controlled atmosphere. In addition, the high-vacuum requirements of the electron gun and high-voltage system require significant re-engineering. Early in-situ systems used gas-tight chambers, sealed with electron-transparent windows [29]. However undesirable properties of this setup, such as additional electron scattering from the window media and permeation of gases into the microscope column lead to efforts to build dedicated, flexible environmental HRTEM instrumentation, as pioneered by Gai and Boyes [30], in the design and construction of a custom environmental TEM (ETEM). In this work, significant modifications were made to the microscope to facilitate the study of materials in controlled atmospheres while retaining conventional HRTEM imaging resolution and other desirable functions of the original instrument. The engineering modifications included the addition of differential pumping apertures along the column axis and inside the objective lens area, together with the inclusion of additional pumping lines within the objective lens. This instrument represented the first permanent environmental-cell system where the environment around the specimen was transformed into a controlled reaction chamber and has now evolved into a commercial instrument offering pressures up to 20mbar for mixed gas environments. This design has been successfully used in atomic resolution HRTEM studies of a range of materials, under dynamic gas environments, elevated temperatures [31-38] and liquid phases [36]. More recently efforts have been made to refine specimen holders using MEMS technologies to provide in-situ environments [37, 38] (Figure 5).

The additional levels of engineering complexity required for ETEM, and the unavoidable (albeit small) losses in imaging performance for conventional HRTEM, especially when used with the latest aberration-corrected instruments, make the concept of a removal, holder-based in-situ system tractable for realistic pressures and temperatures.

**Figure 5**
A typical in-situ nanoreactor. (a) Schematic cross-section. (b) Optical image of the TEM holder with integrated nanoreactor and electrical contacts. (c) Optical image of the nanoreactor membrane, including Pt heating spiral and electron transparent windows. (d) Low magnification TEM image of the electron transparent windows where HRTEM is performed. Reprinted from Ultramicroscopy, 108, J.F. Creemer, S. Helveg, G.H. Hoveling, S. Ullmann, A.M. Molenbroek, P.H. Sarro, H.W. Zandbergen, Atomic-scale electron microscopy at ambient pressure, 993-998, Copyright (2008), with permission from Elsevier.

**Figure 6**
Structural evolution of a 7 nm gold nanoparticle in a quasi-molten state. The heater temperature was set to 415°C in Figs (a)-(d) and 450°C in (e) and (f). (a) Initial decahedral structure, (b) rotated decahedral structure with the 5-fold axis inclined normal to the electron beam, (c) distorted icosahedral structure approximately cuboctahedral structure, (e) highly faceted Marks decahedral structure with the 5-fold axis parallel to the illumination, (f) Marks decahedral structure with the 5-fold axis inclined normal to the electron beam. Reprinted from Ultramicroscopy, 110, N.P. Young, M.A. van Huis, H.W. Zandbergen, H. Xu, A.I. Kirkland, Transformations of gold nanoparticles investigated using variable temperature high-resolution transmission electron microscopy, 506-516, Copyright (2010), with permission from Elsevier.
Many of these designs use pre-fabricated electron transparent thin silicon nitride windows to provide a gas-tight reactor cell assembly. The low thermal mass of these systems, leads to a low specific heat capacity that allows for rapid and precise temperature control. These systems have been extensively used in the study of nano-materials with tight parameterization in terms of spatial resolution and temperature, and have provided data for the construction of nano-phase diagrams [39-41] (Figures 6 and 7).

Detectors
Image recording should not impair the overall resolution of HREM data. However, unless the detector used is carefully optimized with respect to microscope operating conditions this element can have a negative effect on overall performance. Historically, photographic plates using one of several possible specialist emulsions were universally used for image recording [42,43] but these have now been largely superseded by digital detectors largely based on charge-coupled devices (CCDs) [44]. These offer particular benefits in that the images are instantly available, quantitatively in digital form and that the camera response is linear over a large dynamic range [45-48]. Their sensitivity is also far higher than that of most photographic emulsions, making single electron detection possible.

Early experiments using CCD chips as direct TEM electron detectors showed that these were not viable as direct detectors due to the sensitivity of the gate oxide to radiation damage [49]. At low energies (<2 keV), this damage can be avoided using back-thinned CCDs [50] but higher energy electrons penetrate through to the active front side. In addition, fast electrons at energies commonly used for HREM imaging lead to rapid saturation of the CCD well capacity after the detection of only a few primary electrons.

For these reasons until recently indirect detection has been employed in cameras used for HRTEM where the fast electrons impinge on a suitable scintillator and the generated light is relayed to the sensor via a lens- or fibre-optical coupling (Figure 8). However, within this complex coupling, scattering of both the primary electrons and the emitted photons in the scintillator occurs. Both of these processes blur the image, attenuating high spatial frequencies.

Electron sensitive imaging plates have also found application as an alternative digital recording media [51]. These consist of a thin embedded layer (~40 μm thick) of a photo-stimulable phosphor. Luminescence is activated post-exposure by a scanning laser in a separate processing system that converts the output light into a digitised electronic signal. The exposed plate can be subsequently erased by exposure to a suitable light source for reuse. These systems provide excellent recording linearity over a wide dynamic range with sensitivity about three times that of photographic emulsions but which is voltage dependent.

Recent experiments by several groups [52-54] have described detectors that use direct injection of primary electrons into solid-state devices leading to substantial increases in both resolution and sensitivity. Several pixelated CMOS based devices have been fabricated including active pixel sensors [54] where the readout electronics and amplification are integrated at the pixel level. These have demonstrated direct electron imaging of sensitive biological material with performance characteristics exceeding indirect CCD devices [53] (Figure 9).

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This article briefly reviews some of the major technological advances in high-resolution transmission electron microscopy over the past 25 years that have contributed to this technique as one of the most important tools in materials characterisation. From the top to the bottom of the electron optical column, these include field-emission sources, aberration correctors, sample environments and new electron detectors.

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Figure 9
HRTEM image of an array of Flock House virus in the cytoplasm of an infected cell recorded using a DED at 120 keV and at a magnification of 0.89 nm per pixel. The scale bar is 100 nm.


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