Material structure, properties, and dynamics through scanning transmission electron microscopy

Stephen J. Pennycook*1, Changjian Li1, Mengsha Li1, Chuhua Tang1, Eiji Okunishi2, Maria Varela3, Young-Min Kim4 and Jae Hyuck Jang5

Abstract

Scanning transmission electron microscopy (STEM) has advanced rapidly in the last decade thanks to the ability to correct the major aberrations of the probe-forming lens. Now, atomic-sized beams are routine, even at accelerating voltages as low as 40 kV, allowing knock-on damage to be minimized in beam sensitive materials. The aberration-corrected probes can contain sufficient current for high-quality, simultaneous, imaging and analysis in multiple modes. Atomic positions can be mapped with picometer precision, revealing ferroelectric domain structures, composition can be mapped by energy-dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS), and charge transfer can be tracked unit cell by unit cell using the EELS fine structure. Furthermore, dynamics of point defects can be investigated through rapid acquisition of multiple image scans. Today STEM has become an indispensable tool for analytical science at the atomic level, providing a whole new level of insights into the complex interplays that control material properties.

Keywords: Scanning transmission electron microscopy, Electron energy loss spectroscopy, Energy loss near-edge fine structure, Energy-dispersive X-ray spectroscopy, Ferroelectric domain structures, Lead-free piezoelectrics, Point defect dynamics, Nanofabrication

Introduction

With the successful correction of lens aberrations, the STEM has become the dominant microscopy technique used today in material research, due to the availability of simultaneous, multiple, imaging and spectroscopic modes. While these benefits have long been appreciated in principle (Crewe 1966; Crewe et al. 1970; Rose 1974), before aberration correction, it was difficult to get sufficient current into the probe for good quality images, nor could spectroscopic signals be obtained at atomic resolution. Aberration correction, bringing smaller, brighter probes, has overcome the historic disadvantage of STEM, that of poor signal to noise ratio (Pennycook and Nellist 2011). In this review, we highlight some recent achievements and applications to materials. More detailed accounts can be found in a number of recent reviews (Pennycook 2015; Oxley et al. 2016; Varela et al. 2017; Gazquez et al. 2017; Li et al. 2017).

Figure 1 shows the principle of STEM. Like a scanning electron microscope, an incident probe is scanned across a sample, but it is thin enough so that the beam is transmitted, then several signals can be detected simultaneously and used to form images with complementary characteristics. The high-angle annular dark-field (HAADF) detector collects Rutherford scattering from the atomic nuclei, producing an image with strong sensitivity to atomic number Z, often called a Z-contrast image. Light columns such as O are only weakly visible in the Z-contrast image, but are seen clearly in a simultaneous bright-field (BF) image or annular bright-field (ABF) image. In perovskites and related materials, this allows the octahedral rotations to be determined, which are crucial to understanding their properties. If the bright-field detector is removed, electrons can be passed...
through a magnetic sector electron energy loss spectrometer to provide elemental maps and electronic structure information.

**Imaging and spectroscopic modes**

**Imaging modes**

The HAADF image is an incoherent image, that is, a direct image, of the columnar scattering power (Pennycook and Boanter 1988; Pennycook and Jesson 1990; Pennycook and Jesson 1991). It is least sensitive to crystal tilts, specimen thickness, and residual aberrations; therefore, it can provide positions of high-Z columns with high accuracy, as demonstrated in Fig. 2 showing BiFeO₃ (BFO) viewed along the pseudocubic [110] direction (denoted [110]ₚc). However, for O columns, which scatter weakly to the HAADF detector, a bright-field image gives more accurate positions, although, being a phase-contrast image, the correct defocus and thickness combination must be determined by image simulation. Combining the positions from both (simultaneously acquired) images allows the octahedral rotations to be accurately measured (Wang et al. 2016; Kim et al. 2017).

The annular bright-field image, a phase-contrast image first proposed by Rose, (Rose 1974) has also become popular in the aberration-corrected era for imaging light atoms (Findlay et al. 2010; Ishikawa et al. 2011). However, the annular bright-field image may be more sensitive to crystal tilts than a normal bright-field image, as seen from the comparison in Fig. 3 (Kim et al. 2017). Figure 4 shows an example of the application to lead-free piezoelectric materials (Wu et al. 2016). It is known that good properties tend to result from an intimate phase mixture on the nanoscale. Engineering composition to have such phase transitions over the correct temperature range can produce high piezoelectric coefficients; therefore, it is of interest to be able to map local ferroelectric displacements cell by cell to track the polarization rotations. Figure 4 reveals a gradual polarization rotation from a rhombohedral phase (displacement along <110>) to a tetragonal phase (displacement along <100>). It is believed that this is indicative of a low-polarization anisotropy which leads to low-domain wall energy and enhanced piezoelectric coefficient (Zheng et al. 2017). There are many other examples of locating atomic columns to picometer accuracy (Borisevich et al. 2010; Borisevich et al. 2010; Kimoto et al. 2010; Chang et al. 2011; Kim et al. 2012; Yankovich et al. 2014; Tang et al. 2015; Dycus et al. 2015; He et al. 2015; Tang et al. 2016).

Besides accurate location of atomic column positions, much progress has also been made in quantifying crystal...
thickness down to the single-unit cell level, based on column intensity, often referred to as atom counting (Ortalan et al. 2010; Katz-Boon et al. 2013; Van Aert et al. 2013; De Backer et al. 2013; Martinez et al. 2014; Jones et al. 2014; Sang et al. 2014; De Backer et al. 2015). Figure 5 shows an example for a gold crystal (LeBeau et al. 2010). It is even possible to locate an impurity atom in depth with single-unit cell accuracy by accurate fitting of image intensity to simulations (Hwang et al. 2013; Ishikawa et al. 2014). The use of multiple annular detectors provides additional information (Zhang et al. 2015), and recently, it has even been possible to locate vacancies using such quantitative techniques (Kim et al. 2016).

More complex detector geometries are also becoming popular, particularly a segmented detector which allows a differential phase-contrast (DPC) mode (Shibata et al. 2012; Müller et al. 2014; Lazic et al. 2016). Forming the difference signal between opposite segments provides a measure of beam deflection, which can be used to form an image of electric or magnetic fields. Figure 6 shows the imaging of atomic electric fields in SrTiO$_3$, where the fields are seen to point radially outwards from the centers of all the atomic columns, representing the field between the nuclei and the electrons projected along the viewing direction.

A pixeled detector provides another degree of freedom, in that the entire scattered electron distribution can be recorded for each point in the image. Often referred to as 4D STEM, there are several big advantages although at present, the detector readout severely limits the image speed. One major advantage is that the optimum detection angles can be decided after the image scan, not before as required with scintillator detectors. However, a more fundamental advantage is that not just annuli or segments can be used, but more complex detector patterns. This forms the basis of ptychography, where only those regions that give rise to a particular spatial frequency in the image are selected, as shown in Fig. 7. The method produces better signal to noise ratio and higher contrast than bright-field imaging since the electrons carrying no signal are excluded. Furthermore, no defocus or aberrations are needed to produce the image, so it is ideally complementary to the HAADF image, as shown in Fig. 8.

**Analytical modes**

Analytical signals such as energy-dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) may be orders of magnitude weaker than imaging signals involving scattered electrons, as they typically involve inner shell excitation, which has a
decreasing cross section with increasing energy loss. Nevertheless, aberration correction allows much larger currents to be focused into atomic-sized probes, as shown in Fig. 9. This fact, combined with major improvements in EDX collection efficiency, have made atomic resolution EDX mapping quite viable, see for example the near-atomically abrupt SrTiO$_3$/LaAlO$_3$ interface mapped in Fig. 10.

EELS images generally have better statistics because EELS scattering is forward peaked, and for edges not too high in energy, all the inelastically scattered electrons can enter the spectrometer. Hence, it is possible to identify single impurity atoms embedded within a crystal. Figure 11 shows a 0.1% La-doped film of CaTiO$_3$ grown on SrTiO$_3$ by pulsed laser deposition. Using the La M edge, single La atoms can be located in specific columns of the CaTiO$_3$ crystal.

EELS edges also carry information on electronic structure since the transitions from the core level to the first available empty states depend on atomic valence and environment. This is particularly useful in transition metal oxides since the edge features are linearly related to transition metal valence. Hence, oxidation states can be directly extracted from atomic resolution images by comparison to standard spectra, for example, the O-K edge of a series of La$_{x}$Ca$_{1-x}$MnO$_3$ compounds with varying $x$, is shown in Fig. 12 (Varela et al. 2009). The first and second peaks can be fitted by Gaussians and parameters such as their ratio or the relative distance between peaks linearly track the Mn oxidation state. This is especially useful for tracking charge transfer across interfaces as shown in Fig. 13, showing EELS data across a La$_{0.7}$Ca$_{0.3}$MnO$_3$/YBa$_2$Cu$_3$O$_{7-x}$/La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO/YBCO/LCMO) trilayer (Varela et al. 2017). By quantifying the fine structure, the valence
profile can be extracted, and it shows the LCMO layers have a hole concentration slightly higher than bulk while the YBCO layers have a depressed hole concentration, Fig. 14. Hence, electrons have transferred from the LCMO into the YBCO, which is consistent with their respective work functions and explains the depressed critical temperatures in the superconductor (Salafranca et al. 2014). Note also how the normalized pre-peak intensity is higher on the Cu-O planes than on the chains, reflecting directly that the holes responsible for superconductivity reside in the planes.

Another recent major advance is in higher energy resolution, achieved through monochromation, which is reaching into the meV range (Krivanek et al. 2014), opening the door to phonon spectroscopy (Lagos et al. 2017), and bandgap mapping (Lin et al. 2016). Such energy resolution is comparable to that of a synchrotron, but the microscope provides much better spatial resolution.

However, especially for low losses, the spatial resolution of EELS images may not be as high as for the HAADF or EDX image because electrons only need to pass close enough to the atom to cause an electronic transition, which can occur some distance away, an effect known as delocalization. Egerton (Egerton 2008) has introduced a measure of delocalization as the diameter containing 50% of the excitations, \(d_{50}\). However, it should be noted that this is not the same as image resolution, which is best defined as the full-width-half-maximum of the inelastic image (Oxley et al. 2016). Because of the delocalization effect, EELS images tend to have long tails more resembling a Lorentzian distribution than a Gaussian. The extended tails reduce image contrast more than they reduce resolution. Note also that delocalization is not a simple function of energy loss but depends on the actual electronic transitions. Recently, several examples have been found where low loss images show atomic resolution (Zhou et al. 2012; Zhou et al. 2012; Zhou et al. 2012). Quantum mechanical simulations show that such contrast arises from specific high momentum transfer transitions; hence, there is no violation of the uncertainty principle (Prange et al. 2012; Oxley et al. 2014; Kapetanakis et al. 2015; Kapetanakis et al. 2016).

**Dynamics**

The high-energy electron beam can cause ionization of the sample and direct knock-on events (displacement damage). Ionization damage increases as the beam energy is reduced, but knock-on damage decreases, until it
Fig. 8 Simultaneous Z-contrast and phase images of a double-wall carbon nanotube peapod. a Incoherent Z-contrast ADF image clearly shows the locations of the single iodine atoms indicated by the arrows. b The reconstructed phase image shows the presence of fullerenes inside the nanotube. c Annotated phase image with the fullerenes labeled using dotted circles and iodine atoms labeled using cross marks based on their locations in the ADF image. It is clear that the iodine atoms are located close to but outside the fullerenes. For comparison, conventional phase-contrast images including BF, ABF, DPC, and the DPC using the center of mass approach were synthesized from the data and shown in d–h, respectively. The detector area of each imaging method is shown in white color in d–g. The experiment was performed at an electron probe current of ~2.8 pA, pixel dwell time of 0.25 ms and a dose of ~1.3 $10^4$ eÅ$^{-2}$. Scale bar, 1 nm; the gray scale of the phase in b is in units of radians reproduced from Rutte et al. 2016.

Fig. 9 Variation of probe current with probe size for uncorrected, third- and fifth-order-corrected 300 kV microscopes assuming a source brightness of $3 \times 10^9$ A sr$^{-1}$ cm$^{-2}$. Below the green line, the probe is predominantly coherent whereas above it is predominantly incoherent. Adapted from Pennycook 2016, with permission from Springer Nature. Copyright 2016.

Fig. 10 EDX images of a near-atomically abrupt SrTiO$_3$/LaAlO$_3$ interface showing atomic columns identified as labeled, with 10 min total acquisition using an Oxford X-Max 100TLE detector on a JEOL ARM200 equipped with ASCOR aberration corrector operated at 200 kV. The composite image includes all edges except O, top right is the HAADF image. Data courtesy Mengsha Li.
Fig. 11 HAADF image of La-doped CaTiO$_3$ grown on a SrTiO$_3$ substrate with EELS images resolving the Ca, Ti, and O columns, and also revealing individual La atoms. The composite color image shows single La atoms in their respective columns. Data obtained with a Gatan Quantum ER on a JEOL ARM 200F equipped with ASCOR aberration corrector operated at 200 kV, recorded and processed by E. Okunishi.

Fig. 12 a O K edges for a series of La$_x$Ca$_{1-x}$MnO$_3$ compounds with $x=1$, 0.7, 0.55, 0.33, and $x=0$ from bottom to top. The energy scale has been shifted, so the pre-peaks are aligned, and the intensity normalized. The spectra have been displaced vertically for clarity. b O K EEL spectrum showing the Gaussian curves used to extract peak intensity and position (pre-peak in red and main peak in blue). c Normalized pre-peak intensity versus nominal oxidation state for the series of LCMO samples. The dashed line is a linear fit to the data. d Energy separation (calculated as the difference between positions of the second peak and the pre-peak) as a function of the Mn nominal oxidation state for the sample set of samples. Reprinted with permission from Varela et al. 2009. Copyright 2009 by the American Physical Society.
disappears entirely below a certain threshold. Historically such processes have been viewed as undesirable damage events, but now that atomic resolution is possible at lower accelerating voltages, there have been many reports of watching atoms move under the beam, allowing insights into atomic motion and the energy landscape of small particles (Kurasch et al. 2012; Komsa et al. 2012; Komsa et al. 2013; Lin et al. 2014; Yang et al. 2014; Guo et al. 2014; Lehtinen et al. 2015; Jesse et al. 2015). Figure 15 shows a time-sequence of images of a Si₆ cluster images at 60 keV beam energy. This is too low to knock atoms out of the cluster, but is sufficient to induce structural changes—one atom is repeatedly seen jumping from the left to right. Such studies reveal metastable configurations that would not be seen by simply heating the material.

Another interesting insight into the dynamics of vacancies is revealed in Fig. 16, which shows beam-induced oxygen vacancy ordering in a LaCoO₃/SrTiO₃ (LCO/STO) superlattice (Jang et al. 2017). When O
vacancies order into specific lattice planes, the strain energy is reduced since the lattice spacing of an entire plane can relax. The plane containing the vacancies expands, causing dark contrast in a Z-contrast image (Kim et al. 2012). Tracking planar spacings can therefore reveal this ordering process quantitatively. Since the average spacing in the LCO block in Fig. 16 does not change, the images show ordering of pre-existing vacancies rather than generation of new ones.

An example of the beam-induced diffusion of a heavy Ce atom is shown in Fig. 17. Quantification of image intensities matched to image simulations show that the atom jumps between next-neighbor sites inside the crystal, so the beam-induced motion is seeing the same diffusion processes that are normally induced thermally. Correlated vacancy/Ce atom motion and interstitial knock-out processes have also been seen (Ishikawa et al. 2014). The electron beam can even be used for solid-
phase epitaxial crystallization of an amorphous material, as demonstrated by writing the letters ORNL in SrTiO$_3$, see Fig. 18 (Jesse et al. 2015). Such beam-induced nano-lithography should be achievable in three dimensions, due to the nanometer depth of focus of the aberration-corrected probe. Recently, it has been demonstrated that the STEM probe can be used to “push” single impurity atoms through the graphene lattice (Dyck et al. 2017). The potential for single atom fabrication with beams and probes is the subject of a recent issue of MRS Bulletin (Pennycook and Kalinin 2017).

**Imaging, analysis, and nanofabrication in 3D**

Ideally, we need atomic scale imaging, analysis, and nanofabrication not just in a two-dimensional projection but in three dimensions. In recent years, much progress has been made in tomography, combining views in multiple directions to reconstruct 3D structure (Goris et al. 2013; Bals et al. 2014; Goris et al. 2015; Miao et al. 2016; Bals et al. 2016). Figure 19 shows an example of the atomic scale reconstruction of an FePt nanoparticle revealing the presence of different ordered structures and different degrees of ordering (Yang et al. 2017). Grain boundaries and even point defects could be detected. Notable progress has also been made in EELS and EDX tomography, although atomic resolution remains far off due to the lower signal levels (Jarausch et al. 2009; Yedra et al. 2012; Haberfehlner et al. 2014; Collins and Midgley 2017).

The example shown in Fig. 19 required many hours of data collection, which many samples could not withstand. An alternative method is optical sectioning. Aberration correctors achieve higher resolution through higher probe convergence angles. Lateral resolution increases linearly with increasing probe angle; however, depth resolution increases quadratically. So, with the latest generation of aberration correctors, the depth of focus has reduced to the nanometer scale, and the image comes from a thin section of the sample. Changing the focus gives a series of images at different depths which could also be reconstructed into a 3D image without the need to tilt the sample. At present, such optical sectioning has not achieved atomic resolution, but may with future generations of aberration corrector (Pennycook and Kalinin 2014; Pennycook 2015; Ishikawa et al. 2016). Figure 20 shows a simulated focal series of Ce atoms substituted in AlN for probe-forming angles of 30, 60, and 100 mrad (Ishikawa et al. 2015). For the larger probe angles, the two dopant atoms can be easily located at 2- and 8-nm depth. Although these simulations assume aberration-free conditions, simulations including chromatic aberration and the effects of electron shot noise...
suggest this approach should work under realistic conditions (Ishikawa et al. 2016). Optical sectioning can also be applied to analytical signals with nanoscale resolution, avoiding the need for specimen tilting (Pennycook et al. 2017). Alternatively, it may prove better to combine depth sectioning with discrete tomography (Alania et al. 2017).

Conclusions

STEM has developed dramatically in recent years, thanks to the development of aberration correctors which have allowed the advantages of multiple, simultaneous imaging and spectroscopic modes to be exploited with high sensitivity and precision. There are advantages also for in situ and *operando* studies since STEM allows good control of dose rate and illumination area (Chang et al. 2011; Jungiophann et al. 2012; Mehdi et al. 2015; Wang et al. 2016). There are also major developments in mathematical image reconstruction techniques, learning from other fields such as computer vision, which are pushing towards lower dose imaging (Stevens et al. 2014; Meyer et al. 2014; Kovarik et al. 2016; Voyles 2017). It is certainly an exciting and rewarding time to be exploring the atomic world.

Acknowledgements

All authors are grateful to their collaborators on the work cited here. SJP is grateful to the National University of Singapore for funding. CJL is supported by a Lee Kuan Yew Fellowship. Research at Universidad Complutense is sponsored by the European Research Council PoC-2016 POLAR-EM and Spanish MINECO-FEDER MAT2015-66888-C3-3-R. YMK was supported by the Institute for Basic Science (IBS-R011-D1) and Creative Materials Discovery Program through the NRF (National Research Foundation of Korea) grant (NRF-2015M3D1A1070672). J.H. Jang is supported by the Korea Basic Science Institute grant (T37210).

Funding

SJP is grateful to the National University of Singapore for funding. CJL is supported by a Lee Kuan Yew Fellowship. Research at Universidad Complutense is sponsored by the European Research Council PoC-2016 POLAR-EM and Spanish MINECO-FEDER MAT2015-66888-C3-3-R. YMK was supported by the Institute for Basic Science (IBS-R011-D1) and Creative Materials Discovery Program through the NRF (National Research Foundation of Korea) grant (NRF-2015M3D1A1070672). J.H. Jang is supported by the Korea Basic Science Institute grant (T37210).

Availability of data and materials

Not applicable

Authors’ contributions

All authors contributed to the results reviewed, and all authors have approved the manuscript for submission.
Yang Z, Yin L, Lee J, et al. Direct observation of atomic dynamics and silicon doping at a topological defect in graphene. Angew Chem Int Edit. 2014;53:8908–12. https://doi.org/10.1002/anie.201403382.

Yankovich AB, Berkels B, Dahmen W, et al. Picometre-precision analysis of scanning transmission electron microscopy images of platinum nanocatalysts. Nat Commun. 2014;5:1–7. https://doi.org/10.1038/ncomms5155.

Yedra L, Eijarrat A, Arenal R, et al. EEL spectroscopic tomography towards a new dimension in nanomaterials analysis. Ultramicroscopy. 2012;122:12–17. https://doi.org/10.1016/j.ultramic.2012.07.020.

Zhang JY, Hwang J, Isaac BJ, Stemmer S. Variable-angle high-angle annular dark-field imaging: application to three-dimensional dopant atom profiling. Sci Rep. 2015;1:1–10. https://doi.org/10.1038/srep12419.

Zheng T, Wu H, Yuan Y, et al. The structural origin of enhanced piezoelectric performance and stability in lead free ceramics. Energy Environ Sci. 2017;10:528–37. https://doi.org/10.1039/C6EE03597C.

Zhou W, Lee J, Nanda J, et al. Atomically localized plasmon enhancement in monolayer graphene. Nat Nanotechnol. 2012;7:161–5. https://doi.org/10.1038/NNANO.2011.252.

Zhou W, Oxley MP, Lupini AR, et al. Single atom microscopy. Microsc Anal. 2012;18:1342–54. https://doi.org/10.1017/S1431927612013335.

Zhou W, Pennycook SJ, Idrobo J-C. Localization of inelastic electron scattering in the low-loss energy regime. Ultramicroscopy. 2012;119:51–6. https://doi.org/10.1016/j.ultramic.2011.11.013.