Aberration-corrected scanning transmission electron microscopy of semiconductors

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Abstract. The scanning transmission electron microscope (STEM) has been able to image individual heavy atoms in a light matrix for some time. It is now able to do much more: it can resolve individual atoms as light as boron in monolayer materials; image atomic columns as light as hydrogen, identify the chemical type of individual isolated atoms from the intensity of their annular dark field (ADF) image and by electron energy loss spectroscopy (EELS); and map elemental composition at atomic resolution by EELS and energy-dispersive X-ray spectroscopy (EDXS). It can even map electronic states, also by EELS, at atomic resolution. The instrumentation developments that have made this level of performance possible are reviewed, and examples of applications to semiconductors and oxides are shown.

1. Introduction
The performance of scanning transmission electron microscopes has grown very considerably in the last decade. In 2002, a sub-Å electron probe was formed for the first time in an electron microscope [1]. Now there are more than 100 STEMs in the world capable of forming such probes, and probe sizes of the order of 0.5 Å have been reached [2-4]. In 2004, a single atom in a crystalline solid was identified spectroscopically for the first time [5]; now elemental maps with single atomic resolution and sometimes also single-atom sensitivity have been produced in several laboratories, using three types of signals: EELS, EDXS, and quantitative analysis of annular dark field (ADF) intensities. Here we review these developments from the perspective of what they are likely to mean for the microscopy of semiconductors.

2. Modern STEM instruments
The method employed by a STEM to analyze samples is very simple: form a small but intense probe of electrons, scan it over a thin sample, and record various signals that originate from the scattering of the incident electrons by the sample. Atomic resolution and sensitivity are possible because of two key facts: electrons can be focused into a probe that is smaller than one atom, and they interact rather strongly with matter, producing a detectable signal from every atom in a sample.

The STEM’s ultimate performance is determined by many factors, but three of them are predominant:

i) the electron source, which determines the current that can be packed into a small electron probe,
ii) the quality of the STEM’s optics, which determines how small the probe can ultimately be, and
iii) the quality and variety of the STEM’s detectors, which determine what kinds of signals can be collected and with what efficiency.

Important progress has been made in the last decade on all these fronts. In the area of electron sources, the W(310) cold field emission (CFE) gun, whose theoretical brightness is about 10x higher than that of Schottky guns [6], has been improved to give reduced brightnesses of 3x10⁸ A/(m² sr V) [4], which amounts to a “coherent probe current” [7] of 0.43 nA. This is about 3x larger than the values normally measured for W CFE sources, and there are indications that even higher values are possible. In practical terms, it means that a current of 1 nA can now be packed into a 0.14 nm, 200 keV electron probe [4], a setting that is liable to produce small holes rather quickly in many types of samples. But the increased brightness is very useful when the accelerating energy is reduced to avoid knock-on damage, and it is very welcome indeed when the electron source is equipped with a monochromator, which reduces the probe current substantially.

In the area of electron optics, aberration correctors have improved the ultimate attainable probe size by about 3x, to about 50 pm at 200-300 keV primary energy, and about 100 pm at 60 keV. These advances have been covered in many research articles and several volumes, e.g. [8]. Monochromators capable of reducing the energy spread of the incident beam to about 40 meV have been built [9], and new designs that promise to lower the resolution to about 10 meV have appeared [10]. These developments promise to endow EELS with fundamentally new capabilities.

In the area of detectors, an annular bright field detector has allowed the detection of hydrogen columns in YH₂ [11], and a reconfigurable segmented annular detector has been introduced [12]. The collection efficiency of the EELS signal has been increased to >90% through aberration-corrected post-sample optics [13], and the collection efficiency of energy-dispersive X-ray (EDXS) detectors has been improved about 3x relative to previous detector arrangements, to ~7% (0.9 sr) [14].

Other advances have been realized in the areas of stability, with some STEMs now able to keep the electron probe stable to better than 10 pm r.m.s. relative to the sample [7], low primary energy performance [15, 16], and in the quality of the vacuum at the sample, with pressures in the 10⁻⁸ Pa regime now regularly attained in some STEM instruments [4]. The improved vacuum is making it possible to examine samples longer without running into sample contamination or etching [17].

Acting together, these advances have allowed a wide range of new applications in many areas of materials science. To give just one example, a monolayer of BN containing substitutional impurities has been analyzed atom-by-atom, and the position and chemical identity of every single atom in a significant part of the sample has been determined [18]. The sample was of course rather special: its monolayer nature made atomic identification by measuring ADF intensities possible, and its high resistance to radiation damage (at a primary energy of 60 keV) allowed a high irradiation dose that produced an image with the high signal-to-noise ratio needed for the identification. But the work nevertheless shows that the ultimate goal of resolving and identifying every atom in a solid has now been reached in certain samples, and that the new capabilities are bound to produce many new results.

3. Applications to semiconductors
Investigations of semiconductor materials that are carried out in electron microscopes can be divided into three broad classes: a) investigating the structure of the material and of its defects, b) mapping its composition and c) investigating its electronic properties. The STEM can make major contributions in all the three categories, as shown by the examples below.

Figure 1 shows a high-angle annular dark field (HAADF) image of a PbS quantum dot in polycrystalline ZnS. The key unknown was the size and shape of the quantum dots. Lead being heavier than the other elements present made the PbS dots considerably brighter than the ZnS grains. Just one PbS dot is present in the shown field of view, indicated by the double arrow. It is faceted, and about 2.5 x 4 nm in size. Individual Pb atoms can be seen outside of the dot, both on the ZnS matrix and outside it, on the sample support. These may be an artefact due to ion milling displacing atoms rather than removing them, but they are interesting because they show that single lead atoms were readily visible even though the matrix was not particularly light. Another notable feature of the image
is that despite the fact that several ZnS grains show lattice fringes and are thus diffracting, the incoherent nature of the HAADF image (e.g. [8]) has prevented diffraction effects from introducing major contrast artefacts into the image and allowed the PbS grain to remain clearly visible.

Fig. 1. HAADF image of PbS quantum dot, indicated by two long parallel arrows, in a ZnS matrix. Many lead atoms are visible both within the ZnS matrix and outside; some are marked by single arrows. Fourier transform insert (of a larger image area) shows that spatial frequencies up to 1 Å⁻¹ (arrowed) have been transferred into the image. Nion UltraSTEM200, 200 keV. Sample courtesy Profs F.B. Prinz, U. of Vienna and R. Bosch, Stanford U.

Figure 2 illustrates elemental identification using atomic intensities in ADF images of monolayer graphene with one N and several Si impurities. The nitrogen atom gave an image intensity that was 1.3x higher than the average C atom intensity (after correcting for image contributions due to probe tails [18]) and the nitrogen atoms gave 4x the intensity of carbon. The illumination and collection angles for the image were the same as those used for imaging monolayer BN by us previously [18], and the power law relating the intensity $I_2$ of the atomic image to the atom’s atomic number $Z$ was also the same: $I_2 \propto Z^{1.64}$. The example shows that the ADF signal can be used for accurate elemental mapping, provided that the contribution of each atom to the images of its neighbors is carefully accounted for [18].

Fig. 2. a) ADF images of N and Si atoms substituting for C at and near topological defects in graphene, b) Si decorating a graphene edge. Nion UltraSTEM100, 60 keV. Courtesy Matt Chisholm, ORNL and Venna Krishnan and Gerd Duscher, U. of Tennessee.

Figure 3 shows EELS elemental mapping of high concentration elements. The sample was GaAs, viewed in the [011] projection, in which Ga and As atoms separate into different atomic columns. Ga and As $L_{2,3}$ edges, at 1115 and 1323 eV energy loss respectively, were used for the mapping. They were considerably weaker than edges corresponding to energy losses smaller than 1 keV, but even so, largely because of the efficient coupling of the EELS signal into the spectrometer, the mapping could be carried out at 20 ms per pixel with only 100 pA of beam current, i.e. in 82 s total acquisition time for the 64x64 pixel map. Principal component analysis (PCA) was used to minimize the statistical noise.

Fig. 3. Elemental mapping of GaAs. Nion UltraSTEM100 Gatan Enfina EELS, 100 keV. Courtesy Maria Varela, ORNL and Sergio Molina, U. Cadiz, Spain. (colour online)
EELS delocalization is not a major concern for energy-losses greater than 1 keV when either the illumination or the collection angles (or both) are large [7]. This was the case here, with both angles >30 mr. It is therefore not surprising that the atomic peaks in the EELS map are only slightly less sharp than the ADF ones.

Figure 4 shows elemental mapping of La atoms in a TiO$_2$ matrix [19]. The sample was grown on an LaAlO$_3$ substrate, and this allowed La to penetrate into low-angle grain boundaries in the TiO$_2$. An ADF image is shown along with Ti and La elemental maps, made using the Ti L$_{2,3}$ and La M$_{4,5}$ edges, at 455 and 832 eV respectively. A profile integrated vertically through the combined EELS map (upper right) shows that was there was essentially no La dissolved in the matrix on the left side of the boundary, but that there was La enrichment on the right side of the atomically sharp boundary.

![Fig. 4. EELS mapping of La segregation at a low-angle grain boundary in TiO$_2$ grown on LaAlO$_3$. Nion UltraSTEM100, Gatan Enfina EELS, 100 keV, 100x444 pixel spectrum-image. Courtesy Lena Kourkoutis and David Muller, Cornell U. (colour online)](image)

Figure 5 shows a case of EELS elemental mapping used for structure-determination purposes. The sample was LaMnO$_3$ and elemental maps were obtained at 60 keV primary energy, using the O-K, Mn-L$_{2,3}$ and La-M$_{4,5}$ edges respectively. The ADF image (not shown) was dominated by the signal from the heavy La (Z=57) and Mn (Z=25) columns, and the part of the

![Fig. 5. EELS imaging of oxygen octahedral rotations in LaMnO$_3$. Nion Ultra-STEM100, Gatan Enfina EELS, 60 keV. Courtesy Maria Varela and Stephen Pennycook, ORNL. (colour online)](image)
signal that was produced by the O atoms was not at all clear. The elemental map, however, makes it obvious that the oxygen columns are not laid out in a regular rectangular pattern. Their arrangement corresponds to rotated oxygen octahedra, and it would not be visible without being able to image the oxygen atoms separately from the other atoms present. It needs to be noted, however, that there were also oxygen atoms present in the La columns, and that these were not imaged along with the oxygen-only columns seen in the oxygen image [20]. This was due to the fact that the heavy La atoms rescattered the O EELS signal to high angles, outside the EELS entrance aperture. Detailed image simulations have reproduced the experimental image accurately.

Figure 6 shows the mapping of atomic bonding in EuTiO$_3$ grown on DyScO$_3$ [19]. The figure first shows a “conventional” EELS elemental map of Eu, obtained using the M$_{4,5}$ edge at 1131 eV (a), and a portion of a HAADF image recorded simultaneously (b). It then shows that it is possible to identify two distinct components of the Eu edge, which are shifted by about 2 eV (c). The final part shows a 2D colour map of where the different components identified in the spectrum came from (d), demonstrating that the higher energy loss component occurred only at the interface, in a single atomic layer. It most likely corresponds to a layer of Eu $3^+$ at the interface, with the bulk EuTiO$_3$ layer containing Eu $2^+$. Changes in chemical bonding have been mapped by EELS before [e.g. 21], but not with atomic resolution. The fact that chemical bonding can now be mapped column-by-column shows just how far EELS has managed to progress in recent years.

![Fig. 6. Mapping bonding changes at the EuTiO$_3$/DyScO$_3$ interface through spectroscopic imaging. a) Eu elemental map showing reduced Eu concentration at the interface, b) part of the simultaneously recorded HAADF image, c) evolution of the horizontally averaged Eu-M$_{4,5}$ edge fine structure across the interface and the three components, d) three-component fit to the full spectrum-image. Nion Ultra-STEM100, Gatan Enfina EELS, 100 keV. Courtesy Lena Kourkoutis and David Muller, Cornell U. (colour online)](image-url)

Apart from Figure 3, the examples presented above do not show classical semiconductors. However, their implication is clear: it is now readily possible to explore elemental distributions on the atomic scale, using EELS mapping in the STEM. The major limitations of the technique are that a high electron exposure, of the order of $10^8$-$10^{10}$ electrons/nm$^2$ is needed, but must not lead to the sample undergoing major changes, that the sample must be reasonably thin (typically less than 20 nm), and that not all elements have EELS edges that are good for EELS mapping. Nevertheless, it is easy to see that impurities concentrating at dislocations and other defects in III-V and other semiconductors should be readily identifiable, that it should be possible to analyze the electronic properties of a wide variety of electronic interfaces, and that the strong signal and high efficiency of EELS may ultimately yield elemental maps of dopants with single atom sensitivity.
Elemental mapping using the EDXS signal [14] promises to be nearly as powerful as EELS mapping and will enjoy some advantages, such as being able to examine thicker samples, and having spectra that have better peak-to-background ratios and are simpler to interpret. However, the signal strength and the collection efficiency will be poorer than for EELS, and probably not sufficient to map single atoms reliably [22]. Moreover, with the EDXS energy resolution typically >100 eV, examination of changes in the bonding or in the electronic states of a material will not be possible.

Elemental mapping by quantitative analysis of ADF intensities, which can be done with electron doses about 100x smaller than EELS and EDXS mapping, will probably become the technique of choice for mapping elements in monolayers. In thicker samples, its interpretation will be less clear-cut, but even so it is likely to be a useful technique to fall back on when the sample is radiation-sensitive and the large incident dose typically needed for EELS and EDXS mapping cannot be used.

4. Conclusion
Aberration correction scored two major successes in the 1990s: it corrected the vision of the initially defective Hubble space telescope [23], and it corrected the imaging of electron microscopes. The corrected Hubble telescope opened fundamentally new vistas on the large-scale universe, and aberration-corrected electron microscopes are opening new vistas on the world of atoms. Never before have we been able to image and analyze non-periodic matter with the levels of precision, sensitivity and flexibility that are now possible. It is an exciting time to be working on applying the new instruments to materials problems of major practical significance, such as those found in the semiconductor field, and to be pushing the power of the techniques even further.

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