Acta Crystallographica Section A
Foundations and Advances
ISSN 2053-2733

Received 20 October 2014
Accepted 22 October 2014

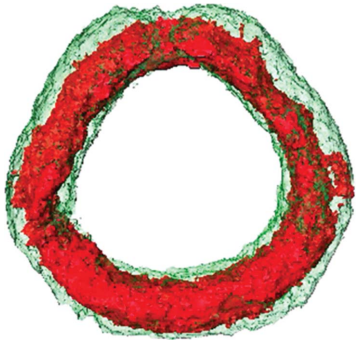
New capabilities for 'colouring in' the chemistry of crystal defects atom-by-atom

Sarah J. Haigh

Material Science Centre, School of Materials, University of Manchester, Manchester, M13 9PL, United Kingdom

'Crystals are like people: it is the defects in them which tend to make them interesting!' It is with these wise words that Professor Sir Colin Humphreys begins his chapter on *Stem Imaging of Crystals and Defects* in *Introduction to Analytical Electron Microscopy* (Humphreys, 1979). Crystal defects such as vacancies, impurities, grain boundaries and dislocations are often crucial for determining the physical and electrical properties of a material. The importance of high-resolution electron microscopy for understanding the detailed structure of crystal defects is exemplified in this issue, where Paulauskas *et al.* report an analytical scanning transmission electron microscope (STEM) investigation of low-energy stair-rod dislocations in CdTe (Paulauskas *et al.*, 2014). Dislocations are known to strongly affect the electronic and optical properties of semiconductor materials, but a detailed understanding of their influence requires structural characterization at the atomic scale.

Aberration-corrected STEM systems are routinely capable of producing sub-ångtröm electron probes with high beam currents (>200 pA), facilitating atomic resolution imaging of a wide range of different materials (Pennycook, 2010; Krivanek *et al.*, 2010). For a pure element, the structure of a dislocation core may be inferred from atomic resolution images, but in compounds a unique interpretation of all atomic positions is more difficult. Combining high-angle annular dark field (HAADF) STEM imaging with electron energy loss spectroscopy (EELS) provides additional compositional information and, by taking advantage of advances in fast data acquisition and spectral processing, this approach allows local atomic scale chemical analysis over large crystal regions (Monkman *et al.*, 2012). Recent complementary advances in STEM monochromator design are pushing the EELS energy resolution to better than 10 meV, which opens up exciting opportunities for exploring previously inaccessible low energy losses (Krivanek *et al.*, 2013, 2014). However, not all materials are ideally suited to EELS analysis. For example, the Cd *L* and Te *L* energy loss peaks have delayed onset edges, resulting in a poor signal-to-noise ratio and often prohibiting atomic resolution analysis of CdTe. In other multi-component systems, overlapping energy loss edges may be difficult to separate effectively.



X-ray energy-dispersive spectroscopy (XEDS) provides an alternative method for obtaining complementary elemental information about a sample, but is often considered a low-spatial-resolution technique. Indeed, until a few years ago, most of the high-resolution electron microscopy community thought of XEDS as EELS's low-resolution 'quick and dirty' cousin: useful for checking the elements present in the sample but not relevant for high-resolution studies and certainly not applicable for single-atom analysis.

The latest XEDS detector systems coupled with high-brightness electron sources, aberration-corrected optics and excellent sample-stage stabilities have demonstrated that these assumptions must be re-evaluated. Single-atom XEDS analysis was first applied to identification of single dopant atoms on graphene

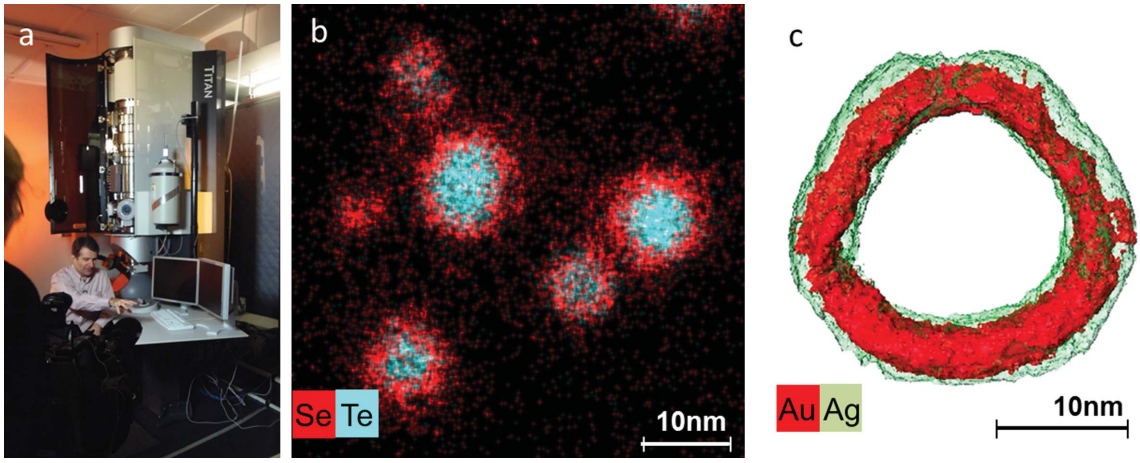


Figure 1
(*a*) Aberration-corrected FEI Titan G2 80–200 kV scanning transmission electron microscope equipped with the 'Super-X' XEDS detector system at the University of Manchester (being filmed for the BBC News). (*b*) Composite XEDS elemental map obtained for a sample of quantum dots and revealing a core-shell morphology [unpublished data similar to the sample shown in McElroy *et al.* (2014)]. (*c*) Tomographic XEDS elemental data set revealing the three-dimensional compositional segregation within an individual Au–Ag nanoparticle. [Reprinted with permission from Slater *et al.* (2014). Copyright (2014) American Chemical Society.]

(Lovejoy *et al.*, 2012). Modern XEDS systems employ large-area silicon drift detectors (SDDs) and/or multiple detector crystals so as to achieve solid collection angles greater than 1 sr (Zaluzec, 2010, 2013), representing an order of magnitude improvement compared to traditional detector designs. Symmetrical arrangements of detectors have facilitated a resurgence in XEDS tomographic imaging (Slater *et al.*, 2014) (Fig. 1*c*), as well as the application of XEDS analysis to *in situ* analysis of nanomaterials in liquids using modified environmental cell specimen holders (Lewis *et al.*, 2014). Improved-efficiency XEDS detectors have reduced the acquisition time and electron dose required for XEDS elemental mapping and thus enabled new possibilities for compositional mapping of nanomaterials (Fig. 1*b*) as well as atomic resolution elemental analysis (Kotula *et al.*, 2012; Allen *et al.*, 2012; Forbes *et al.*, 2012).

Robust oxide materials like $SrTiO_3$ provide an ideal playground for atomic resolution XEDS spectrum imaging, but application of this approach to more electron-beam-sensitive materials such as CdTe is significantly more challenging. Furthermore, crystal defects can often be less stable than the perfect bulk crystal, and this is one of the reasons why the work of Paulauskas *et al.* is so impressive. Using HAADF STEM combined with XEDS spectrum imaging, Paulauskas *et al.* are able to reveal the atomic structure for a Lomer–Cottrell dislocation loop in CdTe with unprecedented detail. The resolution of the XEDS spectrum imaging allows the atomic species for each atomic column within the dislocation core to be identified and the accompanying HAADF STEM images allow crystallographic analysis of the dislocation's Burgers vector and associated strain field. These results provide essential experimental input for first-principles theoretical calculations and demonstrate the potential of analytical STEM XEDS to reveal previously inaccessible structural information for an important class of semiconductor materials.

References

Allen, L. J., D'Alfonso, A. J., Freitag, B. & Klenov, D. O. (2012). *Mater. Res. Soc. Bull.* **37**, 47–52.
Forbes, B. D., D'Alfonso, A. J., Williams, R. E. A., Srinivasan, R., Fraser, H. L., McComb, D. W., Freitag, B., Klenov, D. O. & Allen, L. J. (2012). *Phys. Rev. B*, **86**, 024108.
Humphreys, C. J. (1979). *Stem imaging of crystals and defects. Introduction to Analytical Electron Microscopy*, edited by J. J. Hren, J. I. Goldstein & D. C. Joy, pp. 305–332. New York: Springer. doi:10.1007/978-1-4757-5581-7_11.
Kotula, P. G., Klenov, D. O. & von Harrach, H. S. (2012). *Microsc. Microanal.* **18**, 691–698.
Krivanek, O. L., Chisholm, M. F., Nicolosi, V., Pennycook, T. J., Corbin, G. J., Dellby, N., Murfitt, M. F., Own, C. S., Szilagyi, Z. S., Oxley, M. P., Pantelides, S. T. & Pennycook, S. J. (2010). *Nature*, **464**, 571–574.
Krivanek, O. L., Lovejoy, T. C., Dellby, N., Aoki, T., Carpenter, R. W., Rez, P., Soignard, E., Zhu, J., Batson, P. E., Lagos, M. J., Egerton, R. F. & Crozier, P. A. (2014). *Nature*, **514**, 209–212.
Krivanek, O. L., Lovejoy, T. C., Dellby, N. & Carpenter, R. W. (2013). *Microscopy*, **62**, 3–21.
Lewis, E. A., Haigh, S. J., Slater, T. J. A., He, Z., Kulzick, M. A., Burke, M. G. & Zaluzec, N. J. (2014). *Chem. Commun.* **50**, 10019–10022.

Lovejoy, T. C., Ramasse, Q. M., Falke, M., Kaeppel, A., Terborg, R., Zan, R., Dellby, N. & Krivanek, O. L. (2012). *Appl. Phys. Lett.* **100**, 154101.
McElroy, N., Page, R. C., Espinbarro-Valazquez, D., Lewis, E., Haigh, S., O'Brien, P. & Binks, D. J. (2014). *Thin Solid Films*, **560**, 65–70.
Monkman, E. J., Adamo, C., Mundy, J. A., Shai, D. E., Harter, J. W., Shen, D., Burganov, B., Muller, D. A., Schlom, D. G. & Shen, K. M. (2012). *Nat. Mater.* **11**, 855–859.
Paulauskas, T., Buurma, C., Colegrove, E., Stafford, B., Guo, Z., Chan, M. K. Y., Sun, C., Kim, M. J., Sivananthan, S. & Klie, R. F. (2014). *Acta Cryst.* A**70**, 524–531.
Pennycook, S. J. (2010). *A scan through the history of STEM. Scanning Transmission Electron Microscopy*, edited by S. J. Pennycook & P. Nellist, pp. 1–90. New York: Springer.
Slater, T. J. A., Macedo, A., Schroeder, S. L. M., Burke, M. G., O'Brien, P., Camargo, P. H. C. & Haigh, S. J. (2014). *Nano Lett.* **14**, 1921–1926.
Zaluzec, N. J. (2010). *Microsc. Microanal.* **16**, 1300–1301.
Zaluzec, N. J. (2013). *Microsc. Microanal.* **19**, S2, 1262–1263.