Nanostructure in technicolor

Atom-by-atom structural and chemical analysis by annular dark-field electron microscopy
Nature **464**, 571-574 (2010) doi:10.1038/nature08879

Authors: Ondrej L. Krivanek, Matthew F. Chisholm, Valeria Nicolosi, Timothy J. Pennycook, George J. Corbin, Niklas Dellby, Matthew F. Murfitt, Christopher S. Own, Zoltan S. Szilagyi, Mark P. Oxley, Sokrates T. Pantelides and Stephen J. Pennycook

Recommended with a commentary by Simon J. L. Billinge, Department of Applied Physics and Applied Mathematics, Columbia University,
and Condensed Matter Physics and Materials Science Department,
Brookhaven National Laboratory.

One of the great hopes for nanotechnology is to self organize atoms into designer nanoscale materials allowing us to dial up material properties to order. A huge bump in the road to this dream, one might argue a bump in the first corner, is our inability to solve atomic structure at the nanoscale, the so-called nanostructure problem [1]. The nanostructure problem is sometimes a surprise to people who are used to seeing high resolution transmission electron microscopy (HRTEM) and scanning tunneling microscopy (STM) images that allow us to "see" atoms directly. Although incredibly useful and impressive as images, from a structural viewpoint these images have a number of deficiencies and do not yield full 3D structural solution. First, they only show the arrangement of atoms on the surface, or a projection of rows of atoms down a high symmetry direction. Second, it is not generally possible to know the chemical species of the observed atoms: atomic resolution microscopy is still in the black-and-white era. However, Krivanek and coworkers [2] have used HRTEM for the first time to take a full color atomic resolution photograph of a single layer of boron nitride.

The challenge in this experiment was to get the requisite resolution with enough signal to detect single atoms (atoms of rather low atomic number no less) from a single layer of BN. Here we are not looking down a column of atoms but at individual atoms. This has been accomplished using the latest generation of aberration corrected scanning transmission electron microscopes (STEM). The normal approach to get chemical information is to then do spectroscopy on the inelastically scattered electrons; however, the inelastic cross-section is too small to get a signal from a single atom, which is why the pictures have hitherto stayed black and white. The use of very tiny

spot-sizes available from the aberration corrected STEM instrument allowed a different approach here, annular dark-field imaging. In this mode the scattering power scales with atomic number, Z, (somewhere in the range $Z^{1.5-1.8}$ [3]. This is now a well established technique known as Z-contrast imaging. What the authors showed is that by carefully measuring the intensity of scattering from each individual atom, it is possible to assign it a chemical identity with great precision. There are statistical variations in the measured intensity due to quantum statistics of the scattering process, but enough atoms are measured in an image that the intensity probability distribution can be determined with good accuracy (the distribution is a histogram of the peak intensities from each atom). Fortunately for the researchers the intensity distributions of the different atoms (B, N, C and O)overlapped only at the level of 4-5 standard deviations, allowing very high certainties to be assigned to the species of each individual atom since its intensity can be assigned unambiguously to a distribution for a particular atom species.

The solution to the problem of coloring-in the photograph turned out to be simple and powerful. It is exciting that, given the right (exceptional) equipment, the imaging and coloring is so straightforward and robust. The authors found carbon and oxygen substitutional defects in the BN layer. They found that the carbon defects always appeared as pairs of C, and that the oxygen defects induced significant (~ 0.14 Å) atomic displacements around them. They also found evidence for Na atoms adsorbed on the surface of the BN.

How revolutionary will these new developments be? That is hard to say right now. The demonstration worked on a single sheet of a micacious refractory material. Can it be applied to a broader range of materials without significant damage? What will we learn from samples that are not a single atomic layer thick? The authors mention the possibility of angular dark field three-dimensional tomography at atomic resolution, but the difficulties of even making this approach happen (a sample of a few atoms has to be accurately rotated without losing it and without it degrading in the beam) are enormously challenging, let alone it becoming a routine characterization technique for materials scientists. Another clue lies in the experiments described in this paper. The carbon defects in the BN structure that were observed in the image appeared at positions where, 2 minutes earlier, a hole had been imaged, which yet earlier had been imaged with no hole. In other words, beam damage from the electron beam blew holes in the sheet that were then filled by carbon and oxygen from the immediate environment. It is color photography, but not completely non-destructive color photography. It is a big step forward to see individual atoms in color, but more

bumps still lie ahead in the road to robust nanostructure characterization and designer materials.

---

[1] S. J. L. Billinge and I. Levin, Science 316, 561 (2007).

[2] O. L. Krivane, M. F. Chisholm, V. Nicolosi, T. J. Pennycook, G. J. Corbin, N. Dellby, M. F. Murtt, C. S. Own, Z. S. Szilagyi, M. P. Oxley, S. T. Pantelides, and S. J. Pennycook, Nature 464, 571 (2010).

[3] P. Hartel, H. Rose, and C. Dignes, Ultramicroscopy 63, 93 (1996).