The Impact of Advanced S/TEM on Atomic Scale Characterisation and Analysis

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ABSTRACT

As the limits of nanotechnology are expanded ever further, so too must we push back the frontiers of imaging and analysis. The need for tools that can deliver new, ultra-high resolution information is driving the development of electron microscopy and spectroscopy to the extremes of performance. For example, aberration-corrected S/TEM gives us the ability to work at sub-angstrom length-scales. This, combined with sharply-defined energy resolution, enables us to acquire information at the single atomic level and gain knowledge of inter-atomic bonding for characterisation of chemical composition, electronic structure and mechanical properties. In addition, there is scope for capturing time-resolved structural transformations with sub-nanometer detail, enabling us to directly observe and understand the dynamics of a range of chemical processes *in situ*. We discuss the advances that have enabled these technological breakthroughs and demonstrate the potential for new insights in nano-characterisation and analysis.

Keywords: atomic resolution, spherical aberration correction, monochromator, S/TEM, EELS

1 INTRODUCTION

The introduction of spherical aberration correctors (C_s-correctors) and monochromators was a major milestone in imaging performance, enabling new application developments in transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) [1-3]. Both the image C_s-corrector for high resolution (HR) TEM imaging and the probe C_s-corrector for HR-STEM enable us to access distances smaller than 0.1nm (1Å) at an acceleration voltage of 300kV. In addition, monochromator technology opened the door for more detailed studies of atomic bonding states and electronic properties of nano-structured devices. The combination of these technologies, along with the development of correctors for chromatic aberration (C_c), give a clear path into the future in ultimate S/TEM applications for the characterisation of materials on the atomic scale [4].

These optical developments must prove their performance in an ever more demanding environment of new applications and material classes. Features such as ample space for the specimen for dynamic experiment holders and high voltage flexibility to optimise the lifetime of the sample in the TEM become important boundary conditions for successful scientific work. Additionally in nanotechnology research, a clear need for understanding dynamic behaviour of nanostructures on the atomic level is growing. In these advanced S/TEM applications, parameters such as temperature, mechanical strain, electronic functions or even gas reactions are needed for characterisation on the nano-scale in order to come to a better understanding of the processes involved.

In this contribution, we will present application examples for C_s-corrector and monochromator results on various materials, along with a discussion of new *in situ* experiments being developed, in order to demonstrate the impact that these advances are having on atomic scale characterization and analysis.

2 CORRECTING FOR SPHERICAL ABERRATION C_S

To begin, we illustrate spherical aberration C_s and the effect of switching on a C_s-corrector in HR-STEM. In this case, a probe corrector helps to reduce blurring of the image.

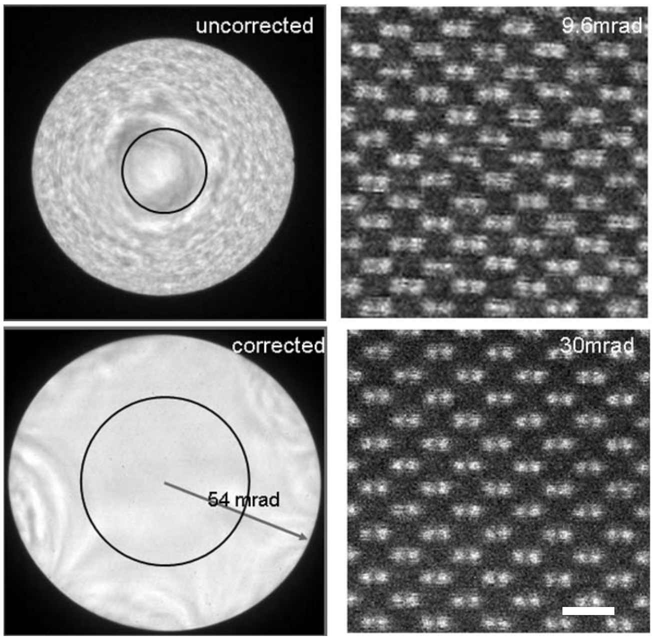

Figure 1 : HAADF HR-STEM image of silicon in <110> direction (right) with Ronchigram image of the imaging condition (left). The upper images were acquired without C_s-correction. Scale bar = 100pm

Figure 1, a high angle annular dark field (HAADF) atomic resolution image, shows silicon in the <110> direction. The circles in the Ronchigram show the convergence angle under which the images were taken. Since the probe size on a C_s-corrected STEM system becomes smaller, so the bright areas of the atoms become smaller in the HAADF image, giving improved resolution.

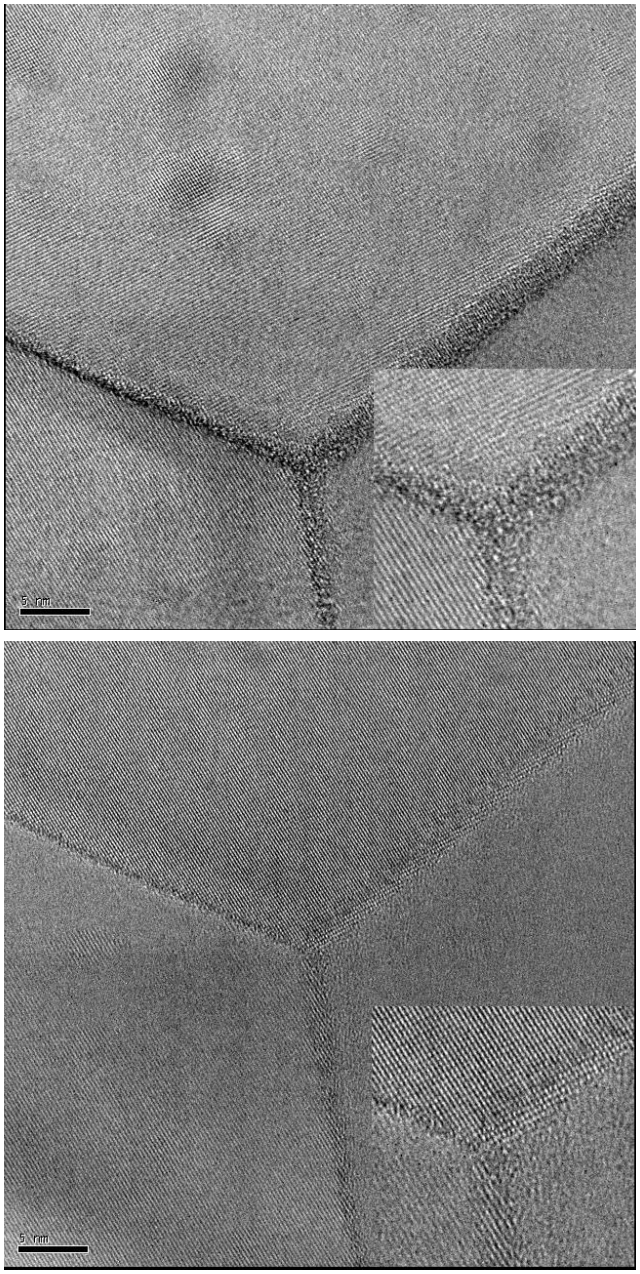

Figure 2 : HR-TEM images of grain boundaries in Al_2O_3. The upper image was acquired without C_s-correction, the lower one with a C_s < 5μm. Scale bar = 5nm. (Specimen courtesy University of Liverpool, UK)

Figure 2 is an example of an HR-TEM image of grain boundaries in polycrystalline Al_2O_3. The C_s corrector works to reduce delocalization of information in the image – a particular problem at interfaces. As Figure 2 shows, the grain boundary in the lower, Cs-corrected image is more clearly discernible, showing the superiority with which we can determine thicknesses of coating layers using image C_s-corrector technology.

3 SENSITIVITY FOR LIGHT ELEMENTS

The sensitivity for imaging ultra light elements can be improved using corrector technology. In figure 3 an HR-TEM image of lanthanum hexaboride, LaB_6, reveals the positions of the boron atoms in the cubic structure and even a contrast difference between a single and double occupied boron position in the unit cell can be detected.

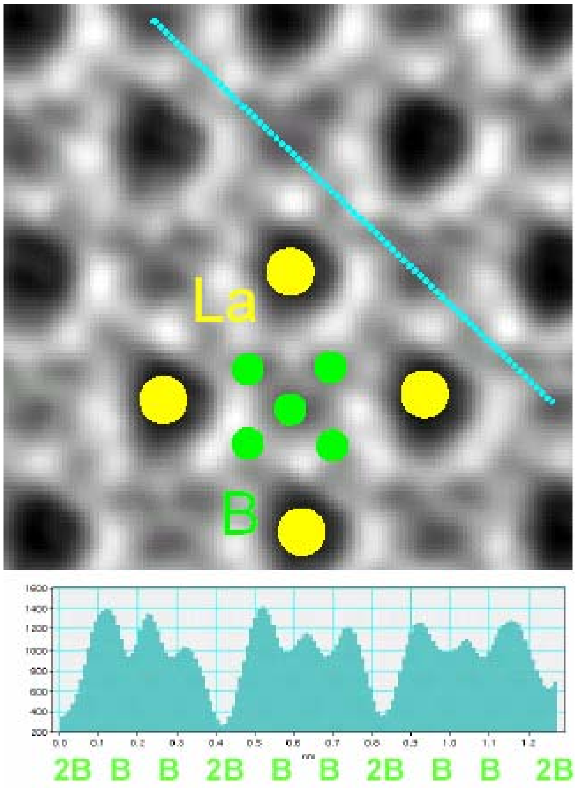

Figure 3 : C_s-corrected HR-TEM image of LaB_6 in the <100> direction. The light boron atoms can be clearly imaged next to the heavy lanthanum atoms. Even a difference in occupancy of two different boron positions in the unit cell can be detected (denoted 2B and B - see profile).

In STEM mode, an electron energy loss spectroscopy (EELS) line scan was taken across 10 unit cells of the same sample. The atomic positions of the lanthanum and boron atoms in the unit cell can be visualized with the EELS signal of the boron-K and La-M edge (Figure 4). This example illustrates the importance of a combination of TEM and STEM examination, in their power to detect the information using complementary signals.

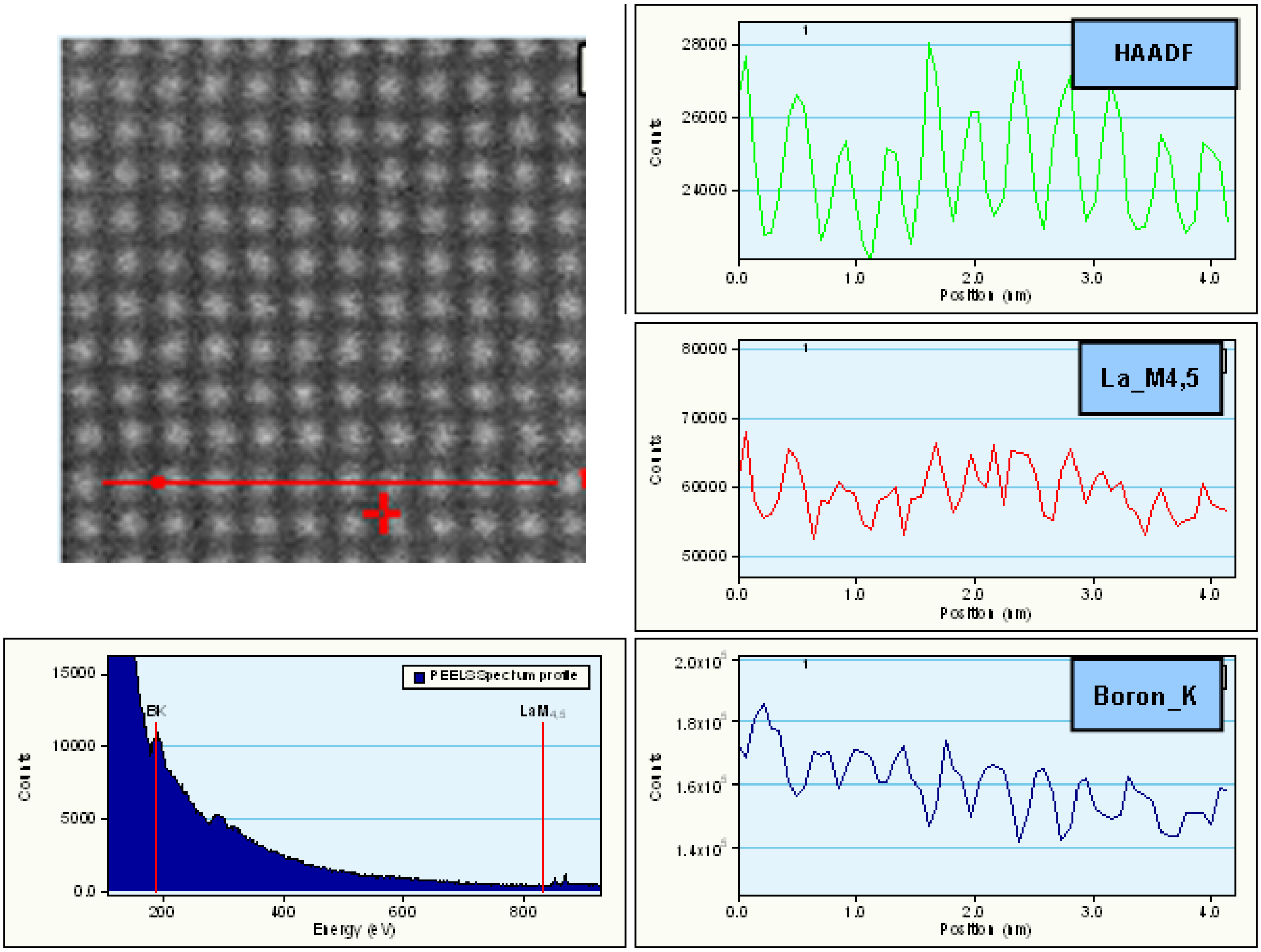

Figure 4 : HAADF STEM image of LaB_6. An EELS line scan across 10 unit cells has been measured. The atomic position of lanthanum and boron atoms in the unit cell can be visualized with the EELS signal of the boron-k and La-M edges

4 MONOCROMATION

Monochromator technology reduces the energy spread of the incident beam, permitting more detailed spectral analysis. This enables us to measure bonding states and electronic structures, like band gaps, optical transitions and dielectric properties with an energy resolution of 0.1-0.2eV. This is comparable with synchrotron sources for EXELFS (extended energy loss fine structure) or EXAFS (extended x-ray absorption fine structure) applications.

Changes in the bonding of silicon in different silicon compounds can be measured in the ELNES (energy loss near-edge structure) data of the silicon K-edge, as shown in figure 5. The major advantage of a monochromated S/TEM is the lateral resolution, even when it cannot compete with the meV range of energy resolution of x-ray instruments. In combination with a probe C_s-corrector this type of information can be principally measured down to the atomic level.

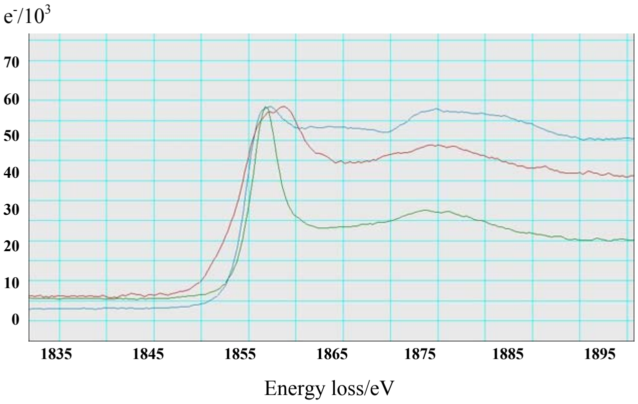

Figure 5 : ELNES measurement on the silicon K-edge (1856eV) for different silicon compounds of a transistor. Pure silicon = blue (upper trace), SiN_xO_y red, SiO_2 = green graph (lower trace)

5 IN SITU DYNAMIC EXPERIMENTS

The increase in resolution offered by aberration correction has another very important consequence: we can increase the working distance, but maintain sufficient resolution, for a host of other applications that require specialized specimen holders and a bit more space in the specimen-lens gap.

One example is ‘environmental TEM’ (ETEM), in which an environmental cell facilitates the flow of gases across a specimen. This enables nanoscale observations of gas-solid interactions, including those at elevated temperatures, such as oxidation, reduction, (de-) hydroxylation, polymerization, nitridation, chemical vapor deposition, growth of carbon nanotubes, self-assembly of nanoparticles and the sintering of catalyst nanoparticles, to name a few. (See, for example, refs [4-10]).

6 CONCLUSIONS

The current nanotechnology revolution is driven primarily by the realisation that atomic and molecular-scale interactions determine the large-scale behaviour of materials. Ready access to imaging and analytical techniques with the atomic-scale (sub-Angstrom) spatial resolution crosses a critical threshold in the nanotechnology roadmap. New instruments, such as FEI’s Titan[1], can now provide clear, unambiguous images of individual atoms. The availability of directly interpretable atomic scale resolution promises to revolutionise nanotechnology.

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[1] The Titan platform is basis of the TEAM project of the USA department of energy with the goal to reach 50pm resolution in TEM and STEM on a single system in combination with C_c-corrector developed in combination with CEOS GMBH