Advances in scanning transmission electron microscopy

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The Pioneer Years
The scanning transmission electron microscope (STEM) was invented by Baron Manfred von Ardenne [1, 2] not long after Max Knoll and Ernst Ruska invented the first transmission electron microscope (TEM) [3], and immediately highlighted the key problem with the technique, that of noise. For high resolution, small probes are needed and the available current is limited. Von Ardenne rapidly abandoned the STEM in favor of Ruska’s TEM design which illuminates a large area, avoiding the issue. It was only when Albert Crewe incorporated a cold field-emission source into the instrument that it became a viable form of microscopy [4, 5]. His field-emission source had orders of magnitude higher brightness, and probes approaching atomic dimensions could carry enough current to form acceptable images. Furthermore, the resolution-controlling optics are before the specimen in the STEM, avoiding many of the chromatic aberration issues in the objective lens, and Crewe also took advantage of the flexible detection optics. Crewe’s STEM was a huge breakthrough; it was the first electron microscope to resolve single atoms [6, 7] (the field-ion microscopy imaged atoms earlier [8]). Crewe’s Chicago group dominated the field, generating a large body of very impressive research results, not only the first single atom imaging, but the introduction of the annular detector, the discrimination of atoms of different atomic number [9], and the first simultaneous annular dark field (ADF) imaging and electron energy loss spectroscopy (EELS) [10], among many others. For a comprehensive review of the activity of the Crewe laboratory see the account by Peter Hawkes [11].

These spectacular breakthroughs stimulated the introduction of a commercial dedicated STEM with a cold field-emission gun by VG Microscopes, which allowed many other laboratories to experiment with the instrument, notably Mick Brown and Archie Howie at the Cavendish Laboratory, University of Cambridge, UK [12, 13], Christian Collieux at the Université Paris-Sud, France [14, 15] and John Cowley at Arizona State University, USA [16, 17]. The author was fortunate enough to be a graduate student, then a postdoctoral scientist at the Cavendish Laboratory with the second VG Microscopes HB5 ever built (the first going to Ron Burge at the University of London). While pioneering for the time, with their UHV cold-field-emission gun and high vacuum, bakeable specimen chamber, digital electronics was in its infancy. Images were recorded on Polaroid or 35-mm film, and EELS data were typically recorded on a chart recorder. Figure 1 shows one of the first EELS spectra to be recorded digitally using a modified Link Systems X-ray multichannel analyzer. The digital acquisition allowed spectra on and off the defect to be subtracted, the first example of a spatial difference technique in EELS [18]. It provided an accurate background subtraction for the N K edge despite the presence of strong extended fine structure variations on the tail of the carbon K loss signal [19].

Z-contrast for materials science
While the Crewe group was primarily interested in biological applications, the other groups had interests in materials science, samples that were typically crystalline. The Z-contrast technique originally introduced by Crewe and coworkers used a ratio between the ADF image (dominated by elastic scattering) and the EELS image (inelastic scattering), which for single atoms had a ratio of approximately Z [20]. However, in crystalline materials diffraction contrast usually dominated such Z-contrast, and the ratio method did not work reliably. The answer was to increase the inner angle of the ADF detector to avoid the domination by coherent Bragg diffraction [12, 21]; the high-angle annular dark field (HAADF) technique was born.

On moving to Oak Ridge National Laboratory (ORNL) in 1982 I applied the HAADF technique to ion-implanted Si, showing how images of dopant distributions could be obtained avoiding strong diffraction contrast [22], and pondered what such an image would look like if the STEM were capable of atomic resolution, would it show incoherent characteristics? Cowley had already obtained a lattice image using a wide-angle, Crewe-style ADF detector [23], although he did not mention any incoherent characteristics, for example, the freedom from contrast reversals which were implicit in the Crewe single atom images, and which had been predicted theoretically for single atoms by Andreas Engel [24]. The question was answered in 1988 when VG Microscopes delivered an HB501UX to ORNL equipped with a high-resolution pole piece. Images of the high-temperature superconductors YBa$_2$Cu$_3$O$_{7-x}$ and ErBa$_2$Cu$_3$O$_{7-x}$ showed both the expected Z-contrast and no contrast reversal with objective lens focus [25]. Images of Si and InP also showed incoherent characteristics, with, more surprisingly, no strong thickness dependence [26, 27]. The reason for the lack of dynamical effects with increasing thickness was because high-angle scattering is dominated by highly localized 1st type Bloch states, and interference with other Bloch states is therefore suppressed. The high-angle detector acted as a quantum state filter. Multislice image simulations were developed based on the frozen phonon method [28], and also predicted almost perfect incoherent image characteristics in crystals [29]. The combination of a simply interpretable...
image with strong Z-contrast uncovered many surprises in the field of interface physics. Rather than fitting image simulations to likely structure models, in many cases it was possible to just look at the image and directly determine the likely structure. Figure 2 shows a photograph of the microscope at ORNL (note the Polaroid camera used to record images) with an interface between CoSi2 and Si showing an unexpected 2x1 interface reconstruction. For reviews of some of these early applications see [30-32]. There was also a push to higher resolution, sub-Å resolution being achieved with John Silcox’s VG microscope at Cornell University [33, 34] and the splitting of the dumbbell in Si<110> with the Cowley VG machine [35]. However, a more attractive route to higher resolution was to use a higher accelerating voltage, as common in TEMs of the day, and VG Microscopes produced four 300 kV STEMs, the HB603 series, one of which, equipped with a high resolution pole piece, was delivered to ORNL in 1993. It resolved the dumbbells in Si and could also distinguish the sublattice in compound semiconductors such as GaAs [36, 37].

Meanwhile, major developments had also been taking place in the technology for EELS, in particular the inefficient serial EELS detectors were being replaced with vastly more efficient parallel detectors [38]. It was natural, therefore, to try out the possibility of achieving EELS with atomic resolution. An efficient charge-coupled-device parallel EELS system was acquired for the ORNL HB501UX microscope from Dennis McMullan, based on a design he produced for the Cavendish VG machine [39]. Despite the small current available in an atomic-sized beam, spectra could be obtained simultaneously with the HAADF signal. This allowed EELS data to be collected plane by plane across an interface using the HAADF signal as a monitor of beam position. To test the possibility of atomic resolution a CoSi2/Si(III) interface was chosen, as such interfaces were commonly atomically abrupt, and indeed the Co L edge disappeared on moving a distance of 2.7 Å from the last plane of the silicide to the first plane in the Si [40]. Shortly after, atomic column resolved EELS was demonstrated at the Si/SiO2 interface [41] and sub-nm resolution mapping of EELS fine structure was achieved [42]. 1993 was a breakthrough year for EELS.

In 1996 VG Microscopes ceased trading, and the increasing demand for STEM capabilities had to be met by the traditional TEM manufacturers. This forced them to bring their STEM performance closer to the theoretical limits [43, 44]. The availability of an efficient STEM mode on commercial TEM columns, complete with full service support, encouraged increasing applications and interest in STEM. For example, the incoherent characteristics and simple mass/thickness image contrast made the HAADF signal ideal as the basis for tomographic reconstruction of three-dimensional (3D) structures [45, 46].

Aberration correction

Incoherent imaging has double the information limit of coherent imaging, (the cutoff being the objective aperture size for incoherent imaging, but the radius for axial phase contrast imaging). However, the triangular nature of the incoherent transfer function means that the contrast is quite weak at the higher spatial frequencies. Together with the ever-present noise problems, Z-contrast images tended to be visually uninspiring. This changed dramatically with the successful correction of lens aberrations [47]. Not only could higher resolutions be achieved, but now the same current could be put into a smaller probe, increasing the image contrast and at the same time improving the signal to noise ratio. The 300 kV STEM at ORNL was fitted with a Nion quadrupole/octupole aberration corrector and achieved the direct imaging of the dumbbell in Si<112> at 0.7 Å [48]. For the first time in history, the STEM was obtaining resolutions higher than the TEM, which is in accord with physics [49, 50] but had previously been impossible due to the noise limitations. EELS saw similar benefits, the first spectroscopic identification of a single atom was achieved with the ORNL HB801UX with a Nion aberration corrector, using the original McMullan parallel detection system [51]. Applications continued to grow in semiconductors, ceramics, complex oxides, catalysis and nanomaterials (for some reviews see [52-54]).

New imaging modes also became possible. For example, aberration correction allowed the objective lens aperture to be opened up, increasing the resolution, but also reducing the depth of field. This could be put to good use, focusing inside materials to locate objects in the third dimension, for example, locating individual stray Hf atoms in the gate dielectric of a semiconductor device structure [55] and the imaging of point defect configurations inside a Si crystal [56]. While the
Figure 4
Atomic structure of a point defect complex in monolayer graphene.
(a) ADF image showing the presence of two dopant atoms.
(b) Simulated ADF image.
(c) Corresponding intensity profiles along X-X’ and Y-Y’ in the experimental and simulated images respectively. Experimental images have been low-pass filtered.
(d-f) Si-L-, C-K-, and N-K- edge maps with blue and green squares indicating the positions of the substitutional Si and N atoms respectively.
Scale bars are 0.2 nm. Reproduced from Ref. 88 with permission.

Figure 5
Z-contrast image of LiFePO$_4$ showing a higher than expected intensity at some Li sites (red circle). EELS from such sites reveals the presence of Fe, and its L$_{2,3}$ ratio is higher than that of Fe in the bulk lattice sites.
Scale bar is 0.5 nm. Reproduced from Ref. 89 with permission.
(MAADF) imaging although it is similar to the original Crewe geometry. Sufficient Z-contrast remains to directly distinguish neighboring light elements, B, C, N and O in monolayer BN for example [85, 86], which is a major advantage over TEM. Atom-by-atom spectroscopy is also possible [87, 88], and an example is shown in Figure 4. Not only are individual atoms identified spectroscopically, they are seen to be substitutional since the carbon elemental map shows an absence of carbon in those regions.

Point defects can now even be probed spectroscopically. Figure 5 shows an example of an antistic defect in LiFePO4. It shows brighter than expected if it contained only Li, and placing the beam on the site an EELS spectrum can be recorded with sufficient signal not only to identify the presence of Fe but to determine its valence. Surprisingly, the valence of the Fe on the Li site is higher than Fe in the bulk lattice, which can be explained by the trapping of mobile Li vacancies [89]. The ability to perform mapping based on EELS fine structure allows not only valence to be mapped, but also new properties. Figure 6 shows how spin states can be mapped in La0.75Sr0.25CoO3 and thin films to reveal the presence of a spin state superlattice, based on changes in the pre-peak on the O K edge [90]. Recently, the localized Cu 3d hole in the 2p plane of La2CuSnO5 was imaged using fine structure on the O K edge [91].

We are also beginning to realize that not all beam-induced changes to the specimen are bad. A gentle provocation can cause the specimen to explore metastable configurations [92, 93]. Density functional theory can then be used to reveal diffusion pathways and other properties. An example is presented in Figure 7, which shows sub-2 nm CdSe nanoclusters that are known to emit white light. This white light emission is remarkable because it occurs even from single nanoclusters, meaning that it cannot simply be explained by an ensemble of clusters with different emission characteristics. Observation in the STEM revealed a continuously changing atomic structure, presumably induced by the beam. We realized that excitation by an ultraviolet photon might also impart enough energy to the cluster to induce a fluxional state. Quantum mechanical molecular dynamics confirmed the conjecture, showing how the fluxionality would lead to a continuously changing band gap, hence the white light emission [94].

These new tools are opening windows onto many areas previously inaccessible. In catalysis it is possible to see the structure of the smallest clusters, and through intensity analysis determine their 3D structure and alloy composition (see Figure 8 [95]). In thermoelectric materials it is possible to see vacancies and how they affect thermal vibration amplitudes [96]. The atomic structures of dopant nanoclusters can be determined within semiconductors [97] and single Au atoms have recently been seen in GaAs nanowires [98] This is just a glimpse of the remarkable new insights now being gained with these techniques into both new and more traditional materials.

Future directions
There are several new directions currently being pursued that will present even more novel opportunities in the future. For example, the ability to obtain probes of atomic dimensions carrying orbital angular momentum offers new possibilities to measure magnetic properties [99]. There is much effort in building in-situ stages that maintain atomic resolution [100] (see for example the ordering of ultrasmall FePt nanoparticles [101]). Furthermore, it is now possible to achieve atomic resolution at one atmosphere [102] and even in liquids [103, 104].

On the instrumental front we see the potential for chromatic aberration correction in STEM, especially at the lower accelerating voltages now in demand where chromatic aberration becomes the limiting factor for spatial resolution [105]. A number of monochromator designs are appearing that would be very appealing if incorporated into an aberration-corrected STEM [106-108], providing the ability to map band gaps and the plasmonic response of nanomaterials [109, 110]. Cathodoluminescence mapping on the STEM is another way to probe optical properties, complementary to EELS, although generally expected to show poorer spatial resolution [111, 112]. It is truly amazing how the STEM has improved in the last 25 years, changing from a dedicated microscope for sub-nanometer analysis to an instrument capable of single atom imaging and spectroscopy with sub-Ångstrom resolution. Surely there can be no better way to unravel the complex functionalities of nanomaterials – every particle is likely to have different structure, different bonding, different impurities and different properties. Examination atom-by-atom, bond-by-bond, in conjunction with local measurements of properties and interpreted through theoretical calculations now offers a new road to understanding the ultimate atomic origins of materials properties.

References
9. Isacson M. et al. Atomic Imaging Using the Dark-


