Benchmarks for a New Era in Quantitative S/TEM: Resolution, Sensitivity and Precision

Bert Freitag, Joerg R. Jinschek and Andy Steinbach, FEI Company, Eindhoven, The Netherlands

INTRODUCTION

The era of widespread commercial availability of sub-angstrom resolution scanning transmission electron microscopy (S/TEM) began in 2005 with the introduction of the Titan platform from FEI. This was the first S/TEM microscope designed from the ground up with the requisite mechanical, electrical, and optical stability capable of fully realizing all the benefits of aberration-corrected electron optics. The motivation to have sub-angstrom performance is given by the challenge in materials science to learn more about the physical properties of materials or devices and how these properties are related to small imperfections at the atomic level. Here, better resolution obtained by corrector technology marks a breakthrough in measuring atomic distance variations or to see defects with higher precision and sensitivity. Additionally, the corrector technology allows adaptation of the high tension to the needs of the material examined to maximize the stability and the contrast of the sample by lowering the voltage. Atomic resolution is still maintained at lower voltages, like 80 kV, and materials unstable in the electron beam at higher voltages (200 or 300 kV) become accessible for electron microscopical studies. These new capabilities are the reason why this microscope has found its way into more than just ultimate atomic resolution, but also to a new era of ultimate quantitative microscopy, where atomic sensitivity, precision, and resolution all play equal roles in enabling new ground-breaking results in materials science.

THE TEAM PROJECT

The TEAM Project has been a collaboration of several Department of Energy-funded groups and two commercial partners, FEI and CEOS. The Project was designed to optimize the S/TEM around aberration-corrected electron optics to further advance the limits of the instrument and the technique. Led by the National Center for Electron Microscopy, the TEAM Project pursued several developments in parallel and comprised two phases – first a "TEAM 0.5" microscope, which

BIOGRAPHY

Bert Freitag studied physics at the University of Cologne, Germany, with an emphasis on solid state physics in metals and superconductors. His PhD thesis at the University of Cologne focused on transmission electron microscopy studies, and he continued with 4 years postdoctoral research in HR STEM and EFTEM/EELS at the Institute for Inorganic Chemistry in the University of Bonn, Germany. He started at FEI Company as an application specialist for STEM products, and his role within FEI evolved to Product Manager for TEM products, and, currently, Product Marketing Manager in the Nanoresearch Market Division responsible for the Titan platform.

ACKNOWLEDGEMENTS

The authors thank the staff and research scientists at the National Center for Electron Microscopy, the TEAM project, and their collaborators for the results reviewed in this article, and Chun-Lin Jia and colleagues at the Ernst Ruska Centre, Jüllich, Germany.

AUTHOR DETAILS

Bert Freitag, FEI Company, Europe NanoPort, Achterweg Noord 5, 5651 GG Eindhoven, The Netherlands
Email: bert.freitag@fei.com

Microscopy and Analysis 23(7):S5-S8 (E U), 2009

A QUANTITATIVE S/TEM
commenced user operations in the fall of 2008, and second a TEAM I microscope, which was successfully completed and commenced user operations on time in October 2009. The TEAM 0.5 instrument is a double spherical aberration (Cₐ) corrected microscope, and is equipped with a special high-brightness gun, a Wien type monochromator, and special measures for stability that are of paramount importance. The new TEAM I instrument aids chromatic aberration image correction hardware to the above technologies. The TEAM Project was funded by the US Department of Energy, Office of Science.

THE PURSUIT OF RESOLUTION AND SENSITIVITY WITH TEAM 0.5

Historically, TEM and STEM imaging resolution have been limited by the coherent Cₐ introduced by the rotationally symmetric electromagnetic lenses used to focus electrons, and also by the incoherent or noise aberrations due to the electrical and mechanical stability limits of the microscope system.

The recent development of practical Cₐ correctors and the introduction of a stable platform dedicated to corrected microscopy have essentially eliminated these limitations. The next obstacle in the quest for better resolution is chromatic aberration (Cₐ), which degrades imaging performance as electrons of different energies are focused at different distances along the column. Cₐ correction to minimize and control chromatic aberration is being employed on TEAM I, but involves a much higher degree of complexity than eliminating Cₐ. By contrast, the TEAM 0.5 microscope employs a tuned monochromator, instead of a Cₐ corrector, to reduce the effects of chromatic aberration by reducing the energy spread of the beam - from 0.8 eV to 0.13 eV at 300 kV, and down to 0.08 eV at 80 kV.

Resolution in STEM imaging is also determined by the spatial coherence, brightness, and total current of the electron emitter source. Improvement of this performance allows reduced exposure times in STEM imaging due to higher signal, which leads to improved usability and throughput and, ultimately, aids resolution improvements, due to reduced sensitivity to any residual mechanical and electromagnetic interferences from the environment. Coherence and brightness depend largely on the type of electron source. Cold field emitters have high energy resolution and brightness, but they have limited total current, and their usability is reduced by the requirement for some level of “flashing” to remove contamination from the tip. By contrast, the Schottky type of field emitter delivers relatively high brightness and very high, very stable current with good energy resolution and no need for tip cleaning procedures. Although cold field emitters have better energy resolution than a Schottky type (with no monochromator), the energy distribution of the cold field emitter is asymmetric and therefore not suitable for the highest energy resolution spectroscopy – an example being low-loss region spectroscopy, such as local bandgap measurements.

In STEM, source brightness determines how much beam current can be squeezed into a small probe for a given applied convergence angle, and therefore is critical to attaining high resolution. In HR-TEM, which is a coherent imaging technique, the coherence of the source and the parallelism of the beam play an important role in creating image contrast and thus enabling information transfer at high resolutions as well. The new high-brightness/high-coherence Schottky field emitter (X-FEG) incorporated in the TEAM 0.5 instrument enables both increased current values in sub-Å scale Cₐ-corrected STEM probes, and improved coherence for boosting resolution in HR-TEM imaging. It is interesting to note that this newly developed electron source has characteristics somewhat analogous to a laser source in the light domain, e.g. a laser has high photon flux that is well-collimated, in combination with its well-known properties of being highly coherent in terms of its optical wave properties. Theoretically, it can be shown that 50 pm resolution requires a brightness after monochromation of >3×10⁸ A cm⁻² sr⁻¹. The high brightness gun and monochromator developed for the TEAM project together deliver an exceptionally high brightness of >5×10⁸ A cm⁻² sr⁻¹ at ΔE = 0.13 eV.

50 PICOMETER RESOLUTION AND SINGLE ATOM SENSITIVITY

Integrated into the ultra-stable TEAM 0.5 column with Cₐ correctors, the X-FEG and monochromator are the final ingredients required to attain 50 pm resolution in both TEM and STEM modes at 300 kV accelerating voltage. Using these, Erni et al. [1] were able to resolve the 47 pm spacing of a Ge <114> crystal imaged with 11%-18% contrast at a 60%-90% confidence level (Figure 1), providing the first direct evidence for sub-50 pm resolution in annular...
darkfield STEM imaging. In a separate experiment, the TEAM 0.5 microscope showed HR-TEM imaging information transfer to better than 50 pm via Young’s fringe measurements of gold nanoparticles on a carbon film [2], thus demonstrating better than 50 pm resolution in STEM and TEM on a single microscope.

Perhaps the most exciting scientific results of the TEAM Project have not been these newly attained resolution benchmarks, but rather the experimental demonstration of what new materials science is now possible with a microscope of such high resolution and signal-to-noise. This sensitivity of the TEAM 0.5 instrument has been used to demonstrate the ability to image and quantitatively detect the signal from single atoms of both high and low atomic numbers.

As an example of the former, Figure 2 shows the results of Kiselevskii et al. [2] showing HR-TEM images of a nanobridge connecting two gold crystals. The images are part of a 15-member focal series recorded in the TEM mode (1.5 exposures at time intervals Δt = 1.5 s, and the four images in Figure 2 show the structural evolution of the crystals over 4.5 s at different focus values. Closer study of the images reveals a wealth of structural changes at the nanobridge/vacuum interfaces that were triggered by electron-beam excitation. The black arrows denote the disappearance of a single gold atom from a two-atom column (Figure 2 a,b), leaving a single gold atom behind (Figure 2 c,d). The red arrows mark a row of thirteen two-atom columns attached to a [111] crystal plane on one edge of the nanobridge. Between exposures, six columns have suddenly disappeared during this short observation time (compare Figures 2c and 2d).

The ability to analyze these images quantitatively in support of these conclusions is demonstrated in Figure 3, which shows a line profile across a two-atom gold column (red line) and a line profile across a single gold atom (black line). Remarkably, the latter single atom profile displays a signal-to-noise ratio of approximately 10, convincingly demonstrating the TEAM 0.5 instrument’s single atom sensitivity in this experiment. The experiment also highlights the interesting possibility of observing in-situ single-atom dynamics using the electron beam as an energy source to both observe and drive the dynamics.

Another investigation involving in-situ single-atom dynamics was recently performed on the TEAM 0.5 instrument by Girit et al. [3] (Figure 4). It demonstrated the ability to image a suspended graphene sheet, whose structure consists of a single layer of carbon atoms bonded in a hexagonal lattice. In this study, the time evolution of a hole in the graphene sheet was recorded, and the dynamics of site-to-site single carbon atom migration within the sheet, and knock-on ejection of single carbon atoms, resulting in a net growth of the hole with time, were clearly observed. Configurations of the sheet’s edge displaying order parameters were observed in real-time, and thus provided confirmation of the theoretical model’s validity. These results were obtained at 80 kV accelerating voltage, which is low enough to avoid immediate disintegration of the sheet, while still providing an energy bath to drive the observed real-time dynamics of carbon atoms at the edge of the hole. Since elastic scattering increases with lower accelerating voltage, the sensitivity is increased at 80 kV for the ultra light single carbon atoms with a good S/N ratio. The combination of the high-brightness monochromated source with the C aberration correction allows sub-Å resolution even at 80 kV, opening up a new era of low voltage sub-Å microscopy, as seen in this work.

**MEASUREMENT PRECISION AT LESS THAN 5 PICOMETERS**

Perhaps the ultimate goal of materials science is the ability to relate the properties and behavior of a material to its detailed atomic structure. Together, the resolution and sensitivity of the new generation of aberration-corrected STEM are enabling measurements of atomic positions and displacements within a crystalline structure with a precision of better than 5 pm. Recent results on the TEAM 0.5 column obtained by Alloyeau et al. [4] demonstrate both single-atom detection sensitivity and precision at the 5 pm level. Figure 5 shows a germanium crystal in [110] projection in an area where the sample is only a few atomic layers thick. In the past, only extended defects such as dislocations and stacking faults could be observed due to resolution and noise limitations, but due to the high sensitivity and resolution well beyond the Rayleigh resolution.
criteria of the 0.14 nm dumbbell distances in Ge (110), direct imaging of single germanium self-interstitial atoms was achieved in this experiment (single-atom Ge interstitials denoted by black arrows in Figure 5). Furthermore, by the use of through-focus series reconstruction and a priori knowledge of the crystal structure, information in the third dimension about the location of these individual interstitials can be extracted and compared with various 3-dimensional theoretical models, some of which predict conflicting results.

Figure 6 shows the extracted positions of individual germanium self-interstitials superimposed within the averaged hexagonal lattice geometry, and compared with various sites theoretically predicted by DFT calculations. Error bars on the mean location of the atoms in the hexagonal germanium lattice averaged over all the unit cells in the measurement set are calculated to be less than 5 pm in standard deviation, giving an unprecedented accuracy for the experimental input to the DFT models, and demonstrating the level of precision obtained in these HR-TEM measurements.

Pioneering materials science results obtained via high-precision quantitative microscopy are also being successfully pursued by a number of leading research institutes beyond the TEAM collaboration. An example is the recent work of Jia and his colleagues [5] at the Ernst Ruska Centre in Jülich, Germany, who used the negative spherical-aberration imaging technique pioneered by their laboratory to study how local atomic displacements generate the local polarizations seen across a domain wall boundary in a PbZr$_{0.2}$Ti$_{0.8}$O$_3$ ferroelectric. Figures 7b and 7c show the structure of this ferroelectric unit cell and the small displacements in the Zr/Ti and oxygen atoms that cause the ferroelectric’s spontaneous dipoles. Figure 7a shows an HR-TEM image with a domain wall (yellow dotted line) and overlaid unit cell projections. The individual atomic positions of the Zr/Ti and oxygen atoms can be clearly seen, indicating a 180° reversal in dipole polarization across the domain wall. By least-squares fitting of all individual atomic intensity profiles around a similar domain boundary, the local experimental values of each unit cell parameter and the shifts of the local Zr/Ti and oxygen atoms were extracted, and an electron optical simulation was employed to eliminate small residual image artifacts. Careful regression analysis showed that the precision of such an analysis was found to be better than 5 pm for a 95% confidence level of the extracted values. Using these measured values the local spontaneous polarization could be calculated, thus realizing the materials scientist’s goal of translating atomic structure into material properties.

CONCLUSIONS

Traditionally, microscopists in materials science have considered a microscope’s resolving power in STEM imaging applications to be the ultimate measure of performance. Clearly resolution is essential to allow direct visualization of atomic scale structures. However, as barriers to resolution, such as spherical and chromatic aberration, have been overcome, additional metrics have emerged as equally important determinants of instrumental performance. First among these are sensitivity and precision. The sensitivity to see single atoms, of both heavy and light elements, brings tremendous value in many research applications. Not only can line defects or interfaces now be seen, but also point defects become accessible via microscopic methods with this increase in sensitivity. Likewise, the precision to measure atomic positions in a crystalline structure to within a few picometers holds great value for many materials science applications.

Many physical properties used in macroscopic devices for various applications have their root cause in the deviation from the ideal crystal position of atoms. Every increase in knowledge due to smaller error bars is of great importance to understand the relationship between structure and these improved properties, which can then enable a breakthrough in technology. Examples are here given in the area such as chemical catalysis, where slightly displaced atoms are often the site of catalytic activity. Together, the three criteria, resolution, sensitivity and precision, form a ‘metrological triangle’ that will largely determine the value of atomic resolution microscopy in nano-technology and energy-related applications, now and into the foreseeable future.

REFERENCES