Depth sectioning with the aberration-corrected scanning transmission electron microscope

Albina Y. Borisevich*, Andrew R. Lupini, and Stephen J. Pennycook

Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

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The ability to correct the aberrations of the probe-forming lens in the scanning transmission electron microscope provides not only a significant improvement in transverse resolution but in addition brings depth resolution at the nanometer scale. Aberration correction therefore opens up the possibility of 3D imaging by optical sectioning. Here we develop a definition for the depth resolution for scanning transmission electron microscope depth sectioning and present initial results from this method. Objects such as catalytic metal clusters and single atoms on various support materials are imaged in three dimensions with a resolution of several nanometers. Effective focal depth is determined by statistical analysis and the contributing factors are discussed. Finally, current challenges and future capabilities available through new instruments are discussed.

aberration correction | electron microscopy | single-atom imaging

The successful implementation of spherical aberration correction in the transmission electron microscope and scanning transmission electron microscope (STEM) is undoubtedly one of the most exciting achievements in electron optics of the last few decades. Correction of magnetic lens aberrations to the third order (1, 2) has led to revolutionary improvements in point resolution and signal-to-noise ratio, expanding the range of accessible lattice spacings into the sub-Ångström regime (3) and enabling simultaneous detection of light and heavy elements (4). Before aberration correction, detection of a single atom was a significant achievement (e.g., refs. 5–8), but now these observations are possible and are even becoming routine for a much wider range of materials (9–11). For a microscope equipped with a high-sensitivity aberration-corrected electron energy loss spectrometer, analytical detection of single atoms within a bulk solid has been reported (12).

However, in addition to improvements to existing techniques, aberration correction can enable completely new experiments to be performed, especially when combined with other new developments, such as environmental or *in situ* stages. In particular, the wider probe-forming aperture available after aberration correction gives a reduced depth of focus. The STEM, largely developed by Crewe and coworkers (13) provides the Z-contrast image mode, which, to a good approximation, gives an incoherent image of the sample (14), making it possible to optically section through a sample in a way similar to confocal optical microscopy (15). However, a significant difference from confocal microscopy is that the STEM technique does not use a collection pin-hole, which degrades the depth sensitivity but is more convenient experimentally. The purpose of this paper is to examine the resolution and contrast for the currently available microscopes and demonstrate how 3D data sets can be collected and analyzed for several test systems.

Results and Discussion

Aberration Correction and Depth of Field. The aberration function χ is defined as the deviation of the aberrated wavefront from an ideal (unaberrated) wavefront such that the phase change across the back focal plane of the objective lens is given by $2\pi\chi/\lambda$, for wavelength λ . In STEM field aberrations are normally ignored,

so this can be written as (omitting nonrotationally symmetric terms) (2)

$$\chi(\theta) = \frac{1}{2} \delta \theta^2 + \frac{1}{4} C_s \theta^4 + \frac{1}{6} C_5 \theta^6 + \frac{1}{8} C_7 \theta^8 + \dots, \quad [1]$$

where θ is the angle to the optical axis, δ is defocus, and C_s , C_5 , and C_7 are rotationally symmetric aberrations of the third, fifth, and seventh order, respectively. In an uncorrected microscope, which uses round magnetic lenses, C_s is always positive (16) and approximately constant under standard conditions, whereas defocus can be varied. Aberration correctors use nonround lenses to enable variation of the aberration coefficients to minimize the aberration function and offset the effect of still higher-order terms. The second-generation aberration correctors installed at Oak Ridge National Laboratory (ORNL) can adjust aberrations up to the third order, whereas future correctors will correct aberrations up to the fifth order or higher (17). The lowest-order uncorrectable aberrations will ultimately determine the optimal aperture size θ which in turn determines the best achievable point resolution. For the case of incoherent imaging, the Rayleigh criterion for the diffraction limited case has the form $\Delta r_{\perp} \approx 0.61\lambda/\theta$, so the resolution scales inversely with the aperture size. Furthermore, increasing the angle θ also affects the depth of field.

The depth of field Δz can be defined numerically in a variety of ways but in incoherent light optics is generally considered to be a range of defocus within which the image contrast does not reduce significantly. Different definitions arise from the different quantitative assessments of what constitutes a significant change of contrast. For example, Born and Wolf (18) suggest the distance within which the intensity on the optic axis stays within 20% of the maximum is a reasonable measure of the focal tolerance. By using the result that for systems with negligible aberrations the intensity on the optic axis obeys the equation

$$I(z) = \left(\frac{\sin\left(\pi \frac{\theta^2}{2\lambda} z\right)}{\pi \frac{\theta^2}{2\lambda} z} \right)^2 I_0, \quad [2]$$

Born and Wolf (18) show that for this criterion the depth of field Δz can be expressed as

$$\Delta z \approx \frac{\lambda}{\theta^2}. \quad [3]$$

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Abbreviations: BF, bright-field; HAADF, high-angle annular dark-field; ORNL, Oak Ridge National Laboratory; STEM, scanning transmission electron microscopy.

*To whom correspondence should be addressed. E-mail: albinab@ornl.gov.

Several frames of a 50-frame focal series collected from TiO_2 powder impregnated with metal nanoparticles (1–3 nm in size and containing Pt and Au at a 1:2 proportion) (19, 20) are given in Fig. 3. High-angle annular dark-field (HAADF) images taken at defocus values of -20 , -88 , and -140 nm (Fig. 3 *a–c*) show completely different arrangements of metal particles on the substrate. In the -20 -nm frame (Fig. 3*a*), a particle in the upper left part of the image (Fig. 3*a*, arrow) appears to be in focus; in the -88 -nm frame (Fig. 3*b*), it is very diffuse, and particles in other parts of the image come into focus (Fig. 3*b*, arrow). In the -140 -nm frame, most of those particles appear diffuse, and yet another particle (Fig. 3*c*, arrow) comes into focus. Notably, the particles denoted by arrows in Fig. 3 *a* and *c* occupy approximately the same lateral position, but they can be clearly resolved in the vertical direction. Fig. 3 *d–f* show the simultaneously collected bright-field (BF) images. Although the general outline of the TiO_2 flakes stays the same throughout the focal series, the flakes closest to focus are identifiable by the appearance of the phase contrast lattice fringes. Each of the three frames has a different TiO_2 particle in focus (shown by the black arrows); the comparison of the HAADF and BF series suggests that in-focus metal particles are attached to the in-focus TiO_2 flakes. We can therefore attempt a reconstruction of the 3D structure of this powder by using the HAADF intensity to identify metal particle positions and the magnitude of the BF contrast to identify the positions of substrate flakes. The resulting 3D representation (derived from all 50 frames in the focal series; see Movie 1, which is published as supporting information on the PNAS web site) is given in Fig. 4. White, transparent surfaces enclose the areas of increased BF contrast and thus represent TiO_2 flakes; yellow surfaces enclose the areas of the increased HAADF intensity and thus correspond to the metal particles. All of the features

Problems similar to the example described in Figs. 3 and 4 are often solved by tilt series STEM tomography, which presently offers superior depth resolution with slightly worse transverse resolution. However, one relevant comparison is that this 50-frame series was recorded in <5 min, although typical tilt series presently take several hours to acquire. More importantly,

Fig. 5. Frames from the HAADF (detector inner angle, 50 mrad) depth series (smoothed raw data) acquired by using a VG HB603U microscope at ORNL on a (Pt, Ru)/ γ -Al₂O₃ catalyst sample at -12 nm (a), -16 nm (b), and -40 nm (c) from initial defocus. See Movie 2 for the full sequence.

tilt-series tomography depends on the validity of the projection approximation (by definition, the depth of field should be greater than the sample thickness) and is therefore constrained to smaller convergence angles, necessarily reducing the point resolution, or requiring extremely thin samples (21). These constraints will become even more limiting for future probes with higher convergence angles, such as the probe on Fig. 1c. Not having these limitations, depth slicing can be used for 3D localization of objects as small as one atom and in objects thicker than the depth of focus, producing models of the imaged samples with depth resolution on the order of several nanometers and atomic resolution laterally, as illustrated in the next example.

Fig. 5 shows several frames from a focal series of a sample of γ -Al₂O₃ powder impregnated with Pt₂Ru₄(CO)₁₈ (22), dried, and mounted on carbon film. The γ -Al₂O₃ flake is off-axis and appears as a pale blur. In the frame taken at a defocus value of -12 nm (Fig. 5a), a thin metal particle (arrow) in the lower right corner appears to be in focus, whereas, in the next frame (defocus -16 nm) (Fig. 5b), it is already out of focus and a thicker particle in the upper left corner (Fig. 5b, arrow) comes into focus instead. Several steps later, at a defocus of -40 nm (Fig. 5c), the γ -Al₂O₃ flakes fade far out of focus, but a single Pt atom (Fig. 5c, arrow) is visible attached to the surface of the underlying carbon film.

Single atoms are visible over several adjacent frames (not shown on Fig. 5; see Movie 2, which is published as supporting information on the PNAS web site), which can thus be used to quantitatively analyze the dependence of the incremental intensity on defocus. For the Pt atom on carbon, the incremental intensity was computed from a 2D Gaussian fit of the 25×25 pixel patches of the image containing the atom. The carbon film

Fig. 6. Variation of the incremental intensity of the single atom from the depth series in Fig. 5 (■). The line is a Gaussian fit.

background was assumed to be flat, and the Pt atom image was assumed to be rotationally symmetric. The resulting dependence is given in Fig. 6. The intensity peaks at approximately -40 nm, but the Pt atom is still quite visible 4 nm away from that defocus; the peak width calculated from Gaussian fit is larger than projected for the probe (full width at 80% maximum of 5.9 nm compared with 3.9 nm; see Fig. 1b). This discrepancy could be due to beam broadening upon passing through the carbon film or just the sparse sampling in the depth direction (4-nm steps). Vertical movement of the sample is also a potential problem. Although it is routinely checked (and found negligible) by reproducing one or more of the initial frames after a series is complete, it cannot be monitored in real time.

Error bars on Fig. 6 are equal to the standard deviation of the intensity of the carbon film background away from the metal atoms. At its peak, the Pt atom in Fig. 5c is $\approx 7\sigma$ above the background, which results in a wide range of visibility over the noise and thus allows us to make a good estimate of the focal depth. Clearly, the signal-to-noise parameters of images, as well as the quantitative settings of acquisition, will play a major role in the range of visibility of point defects and should be taken into account in data analysis. Any experimental determination of the focal depth should be conducted in such a way as to minimize this influence to obtain a reliable result. The effect of the signal-to-noise ratio on the apparent focal depth was also suggested from observation of single Hf atoms within an amorphous SiO₂ layer (23).

It should however be noted that for an isolated object, such as a single heavy atom on a light support, the precision with which the vertical position could be determined is much better than the vertical resolution of the instrument. If there exists independent evidence that the source is a single atom (e.g., by comparison with other single atom intensities and agreement with total concentration) and sufficient quantitative data can be collected to describe the depth dependence of the associated incremental intensity, the vertical position (i.e., peak center) can be determined by fitting with sub-nanometer accuracy. For example, the Pt atom on carbon film in the series from Fig. 5 can be located at the height of $\approx 40.3 \pm 0.2$ nm with 95% confidence.

It should again be emphasized that with currently available instruments these values of resolution and precision are only achievable for heavy atoms/particles on considerably lighter amorphous or nearly amorphous substrates. Superior depth resolution for similar systems will undoubtedly be achieved for new C₃/C₅ corrected instruments with the predicted focal depth of ≈ 1 nm (Fig. 1c). Depth sectioning within aligned crystals is currently out of reach because of electron channeling phenomena (24), meaning the signal from an atom in such a structure depends on the location in a more complicated manner. However, additional simulations show that some depth sectioning in such crystals may become possible in these future instruments, as predicted by Peng *et al.* (25). The simulation details and

implications are discussed in ref. 26. Deconvolution is also a logical next step.

Conclusions

Aberration correction improves the resolution of scanning transmission electron microscopes by enabling higher convergence angles for the STEM probes. Probe simulations show that the increased convergence angles result in a depth sensitivity of currently available aberration-corrected STEM instruments on the nanometer scale; this sensitivity is expected to improve when the next generation of instrumentation is available.

Initial experiments using a 300-kV VG HB603U with a 23-mrad probe angle demonstrate nanometer-scale depth sensitivity on nanocatalyst samples. Nanometer-sized particles and even single atoms can be localized in three dimensions. Statistical analysis of the data are used to quantify the effective focal depth, which is determined by the probe but also affected by sample parameters, such as signal-to-noise ratios, and image acquisition settings. New microscopes with C_3/C_5 correctors are expected to significantly improve the depth resolution in amor-

phous and nanoparticulate materials and enable depth sectioning in aligned crystals.

Materials and Methods

Samples were prepared by dispersing catalytic powders onto holey carbon grids. Before imaging, samples were annealed in vacuum at 100°C for 15 min to reduce carbon contamination. STEM observations were made with VG HB603U microscope operated at 300 kV and equipped with Nion (Kirkland, WA) aberration corrector. The microscope parameters were as follows: probe angle, 23 mrad; HAADF detector inner angle, 50 mrad; BF detector outer angle, 1 mrad.

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