Visions of Atomic-Scale Tomography

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Introduction

A microscope, by definition, provides structural and analytical information about objects that are too small to see with the unaided eye. From the very first microscope, efforts to improve its capabilities and push them to ever-finer length scales have been pursued. In this context, it would seem that the concept of an ultimate microscope would have received much attention by now; but has it really ever been defined? Human knowledge extends to structures on a scale much finer than atoms, so it might seem that a proton-scale microscope or a quark-scale microscope would be the ultimate. However, we argue that an atomic-scale microscope is the ultimate for the following reason: the smallest building block for either synthetic structures or natural structures is the atom. Indeed, humans and nature both engineer structures with atoms, not quarks. So far as we know, all building blocks (atoms) of a given type are identical; it is the assembly of the building blocks that makes a useful structure (see Figure 1). Thus, would a microscope that determines the position and identity of every atom in a structure with high precision and for large volumes be the ultimate microscope? We argue, yes. In this article, we consider how it could be built, and we ponder the answer to the equally important follow-on questions: who would care if it is built, and what could be achieved with it?

Atomic-Scale Tomography

Tomography is a general term used to describe experimental means for determining the internal three-dimensional (3D) structure of objects. The term tomography was coined by Mayer in 1914 [1] to describe the derivation of 3D information from two-dimensional X radiographs. Tomography gained prominence in the 1970s when computational electronics caught up with the need for reconstruction of radiographs, and computer-assisted tomography (CAT) was born. Since then, the term has been applied to many methods. It may be performed on all length scales from the macroscopic to the atomic. At the finest length scale of microscopy, the atomic scale, tomography is discrete [2] and involves the determination of all atom positions and identities. To be technologically useful, it should be applicable to length scales that are large enough to encompass a feature of interest. The larger the field of view, the more materials challenges a microscopy can effectively tackle.

We can thus ascribe the following properties to an ideal tomography at the atomic scale:

1. 100% of the atoms should be positioned and identified.
2. The 3D position of each atom should be determined with precision and accuracy that are sufficient to determine the structure. With high precision, the deviations from perfect structure, that is, defects, should be apparent.
3. The information should cover a large enough volume to be technologically useful. Based on today's standards, this means millions to billions of atoms.

Figure 1: An object may be fully described if the location and identity of each building block is known with precision for the full structure. In this case, this building could be modeled, analyzed, and reconstructed based solely on this knowledge.

These properties define atomic-scale tomography (AST).

What is the Importance of AST?

Today, a single atom in a structure can make the difference between success and failure. For example, the properties of active components in electronic devices made of nanotubes vary markedly with the addition of a single atom. Moreover, the properties of many materials, such as photovoltaic cells, are controlled by their defect populations. Therefore, characterization tools, such as AST, that can detect and identify single atoms and vacancies are critical to laying the scientific foundation for the development of future materials. Complete characterization of point defect populations and the solute environment around each point defect is of interest. Imagine the complexity of first-wall materials and reactor internals with non-equilibrium concentrations of vacancies, interstitials, multi-generational daughter-product isotopes, nanoclusters, precipitates, grain boundaries, and so on. Any strategy for developing materials for these applications will require far more information than is available from today's microscopes.

AST would address this complex problem head on. This form of microscopy demands both 100% detection efficiency for all types of atoms and a 3D spatial resolution sufficient to position each atom precisely on its lattice site. Any missing atoms must be vacancies or voids. Once the individual vacancies are mapped, the solute atoms around each vacancy can be determined. This would enable vacancy-solute interactions to be investigated, which is particularly important for a fundamental understanding of diffusion and kinetic studies, especially under extreme conditions. True atomic-scale characterization of real microstructures would provide an unprecedented understanding of new and existing materials.

Achieving AST

Has AST already been realized? By the definition above, it has not. There are two microscopy techniques that come close to AST: transmission electron microscopy (TEM and scanning TEM [STEM]) and atom probe tomography (APT). TEM/STEM offers high lateral spatial resolution imaging, crystallographic information, and chemical information from electron energy loss spectrometry (EELS) and energy-dispersive X-ray emission spectrometry (EDS). APT offers 3D compositional imaging and analysis at the atomic scale with high analytical sensitivity. Both TEM/STEM [3, 4] and APT [5, 6] have experienced a recent phase of rapid development. These tremendous gains in performance over the past decade give cause to consider whether TEM/STEM or APT can be improved to the point where they deliver AST.

Scanning transmission electron microscopy. The aberration-corrected TEM has sub-Ångstrom spatial resolution in the *x-y* plane and can resolve individual atomic columns in high-resolution TEM (HRTEM) phase-contrast images and in high-angle annular dark field (HAADF) STEM images.

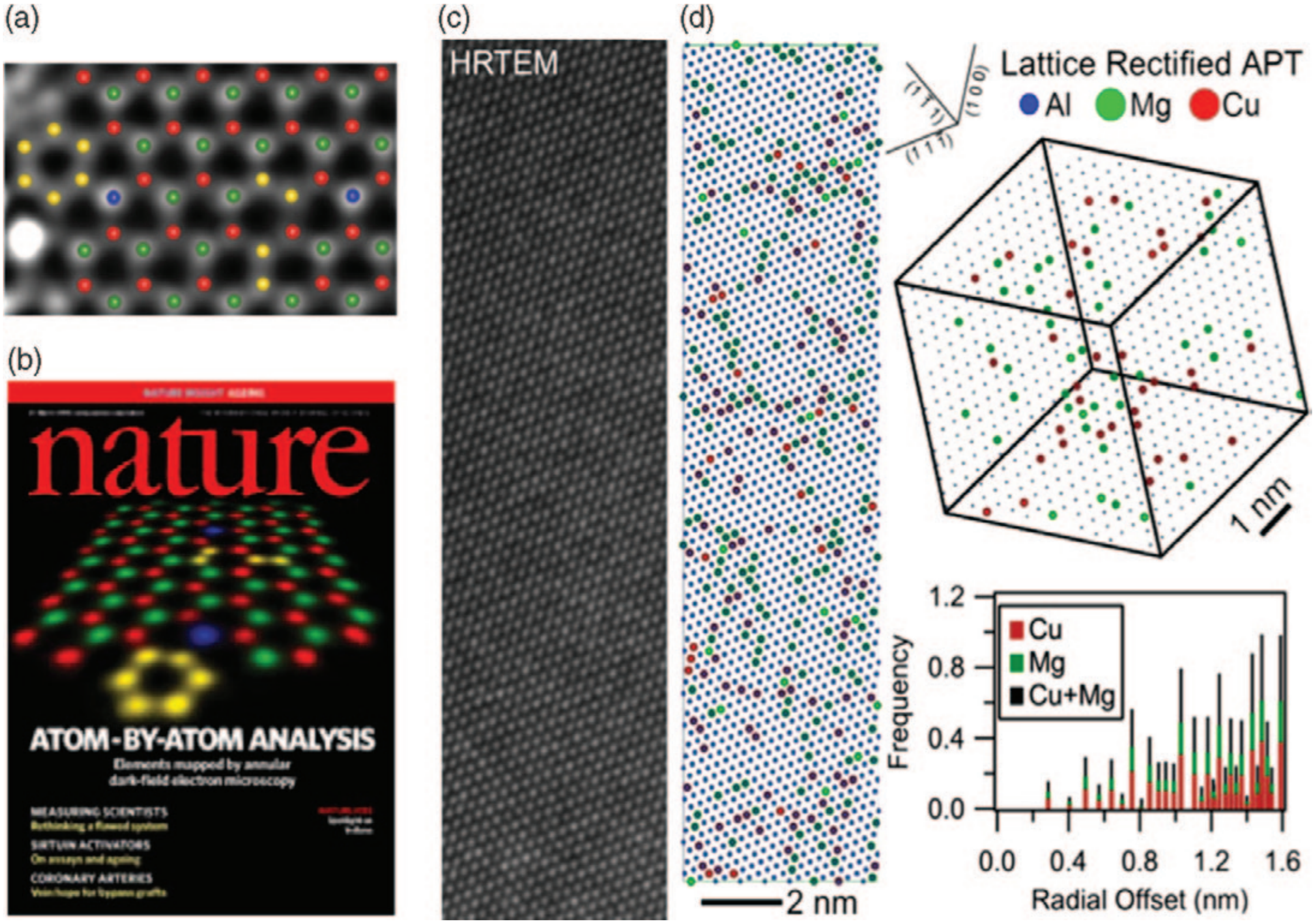

Figure 2: (a) ADF STEM image of the location of different atoms in a monolayer of BN taken in a Nion UltraSTEM. Part of a DFT simulation of a single BN layer containing the experimentally observed substitutional impurities is overlaid on the corresponding part of the experimental image. Red = B, yellow = C, green = N, blue = O atoms. Courtesy of Krivanek et al., 2010. (b) http://www.nature.com/nature/journal/v464/n7288/. (c) HRTEM image of atomic columns in an Al-Mg-Cu structural alloy. (d) Corresponding lattice-rectified APT images showing the distribution of the Mg and Cu solute atoms in 3D [15].

Because the microscope forms projection images through the sample, the spatial resolution in the *z* direction is several orders of magnitude less than in the *x-y* plane. Contrast differences between atomic columns in HRTEM cannot be used reliably to deduce composition differences, but this can be performed in STEM. EELS signals and, in some cases, EDS signals can also provide valuable information of this sort. However, the position of any given atom within a single column is not available. In special two-dimensional (2D) cases, such as monolayers of BN or single sheets of graphene [7], the TEM/STEM can identify individual atoms (see Figures 2a and 2b). Impressive though these 2D atomic-resolution images are, they do not address the critical and fundamental capability of generating atomic resolution in 3D. The challenge is clearly apparent in Figure 2c, which presents an HRTEM image of a structural aluminum alloy. AST information is of great interest in this alloy because the formation of small clusters of about 10 atoms of hardening elements such as Mg and Cu in early stage ageing nearly doubles the strength [8]. This specimen is about ~10 nm thick (~50 atoms) and contains at least 4 elements of interest. Any one column may contain some atoms of each element. It may be possible to measure the column composition with some form of HAADF, EELS, or EDS signal, but the positions of each of the various atoms in the column are not available with this approach. Indeed, the number of atoms in the column is not known to better than 10%.

A path to AST through TEM/STEM might be realized through tomographic analyses based on several atomic-resolution images from low-index poles at large angles to each other. However, the specimen through-thickness in any of these directions must be small (<10 nm), which suggests that the specimen should be a 10 nm diameter needle (or sphere, actually). However, this specimen shape often does not satisfy the requirement for a technologically relevant volume. Even if all of the atoms were positioned accurately in this volume, their identities would not be known in the general case, especially in a non-dilute, non-binary alloy specimen. Thus, TEM/STEM by itself does not appear to offer a path to AST.

Atom probe tomography. APT offers analysts the opportunity to examine inorganic and organic materials with a discreet 3D image made up of detected atoms or small molecules (up to 60% detection efficiency) with high spatial resolution (better than 0.3 nm in all directions), high analytical sensitivity (about 1 atom per million), and over volumes of greater than 10^6 nm^3 (100 nm × 100 nm × 100 nm) containing more than 10^8 atoms. For some complex material structures, however, the reconstruction of the 3D image has severe distortions [9]. For those structures that do not have these problems, the results can be outstanding. A high percentage of the atoms are recorded, but it is not the 100% needed for defect resolution and detection of small numbers of atoms. Though the crystal structure has been measured and found to be consistent with known results in several simple cases for metals [10–12], this is not a general capability of APT at this time.

Lattice-rectified APT data [13–15] approach the ideals of AST, as shown in Figure 2d, where the detailed nature of fine-scale clusters of copper and magnesium solute atoms are resolved within the same alloy [15]. In Figure 2d, the positions of each atom are known in each atomic column; 40% of them have been inferred by lattice rectification in this example. Thus APT offers a great start toward AST, but its shortcomings must be addressed. If the detection efficiency can be improved to 100% and the reconstruction of atom positions can be perfected for most materials, then perhaps AST can be achieved with APT as its basis.

Detecting 100% of the Atoms

Atom probe tomography is limited to less than 100% atomic detection efficiency by technology, not physics. Microchannel plates (MCP) are the first line of amplification of the ions, and they achieve about 60% detection efficiency. Although some attempts have been made to improve the efficiency of MCP detectors [16], their current efficiency is far below the desired level for the detection of all atoms. One possible technology that offers realistic prospects for delivering 100% detection is the superconducting detector [17, 18]. A core property of superconducting detectors, very low binding energy (3–5 meV) of the signal-generating Cooper-paired electrons, is their best attribute for a possible solution. A geometry based on the 2D superconducting metallic strip-line detector [19, 20] has promise.

Superconducting detectors should also be capable of simultaneously measuring the kinetic energy of the field-evaporated ions. This information can be used to discriminate overlapping peaks that have the same mass-to-charge-state ratio but different charge states [18]. If the energy-resolving power is high enough, then it would be possible to know the energy deficit in voltage pulsing and thus obviate the need for energy compensation devices such as reflectrons. Furthermore, laser pulsing could be synchronized with a modest voltage pulse so that evaporation events occur only during times of higher voltage, and the data may then be separated from the background that is primarily produced between pulses. This could enable "noise-free" imaging in APT. A field ion microscope (FIM) imaging gas could then be intentionally introduced because it can be filtered from the data, and this would enable simultaneous FIM and APT. If this prospect is realized, then the key elements of AST, 100% detection efficiency and perfected reconstruction, might be realized through such detectors alone. A conceptual design of a kinetic-energy atom probe (KEAP) instrument is shown in Figure 3. There is no fundamental reason why a detector for

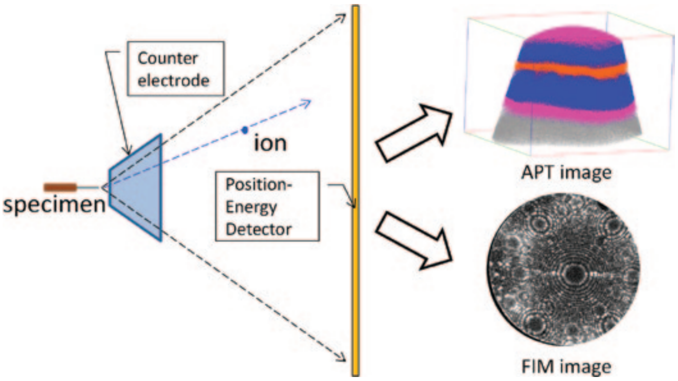

Figure 3: Logical geometry of a KEAP [18]. In addition to ~100% detection efficiency, the position-energy detector would provide kinetic-energy discrimination for ions. The detector would be placed close to the specimen to maximize solid angle. Mass resolving power would be diminished by the short flight times, but peak discrimination would be enhanced significantly overall by the augmentation of time-of-flight spectroscopy with kinetic energy information. Field ions may also be filtered from the data based on energy.

APT that offers 100% detection efficiency for the ions cannot be developed. Whether it is based on superconductors or otherwise remains to be seen.

Perfecting Reconstruction

Is it possible to enhance APT or combine APT with TEM/STEM or another microscopy to improve reconstruction and realize AST? In searching for ways to fix reconstruction in APT, we always come back to the fact that the specimen is the primary optic. The shape of the evaporating surface dictates the ion trajectories. In principle, within the limits set by the case where ions do not cross each other's path, reconstruction of APT data can be perfected with sufficient knowledge of the specimen evaporating-surface shape during an experiment. This means that if we have a way to determine the shape of the specimen evaporating surface with enough precision, then at least the reconstruction imprecisions can be overcome.

There are at least two ways that this information might be obtained experimentally throughout an APT experiment: (1) microscopy of the specimen apex and (2) simulations of field evaporation for model specimens. In practice, these two sources of information may be used together in an operating mode where microscopy provides the starting point for simulation work, which improves the image of the specimen. The improved image becomes the starting point for the next iteration until they converge to a unique solution.

Reconstruction enhancement by STEM. The ATOM Project [21, 22] has been proposed by the authors as an experimental program to develop an instrument dubbed the *atomscope*, which is a local-electrode atom probe inside the objective lens of a UHV STEM, such as the Nion UltraSTEM 200 (Figure 4). This instrument is intended to satisfy, among other things, the need for high-quality information about the specimen apex shape throughout an atom probe experiment for the purpose of perfecting reconstruction. Peterson et al. [23, 24] have developed the surface tangent algorithm (STA) for STEM tomography and have shown it can efficiently and accurately determine the specimen apex shape (see Figure 5). This program would explore the experimental needs for frequency and quality of specimen apex shape determinations in order to perfect reconstruction in atom probe tomography. An advantage of STEM imaging over TEM imaging is that the deflection of the electron beam by the high electric fields at the specimen apex simply alters the location of the transmitted signal in STEM in ways that can be accommodated. Some investigations of this geometry have previously been made [25]. Thus, it appears that a combination of STEM and APT can satisfy the requirements of AST (Table 1).

Reconstruction enhancement by simulation. The role of image simulation in APT is analogous to its role in phase-contrast TEM. Both systems rely on feedforward models that hope to achieve closure by image matching [22]. It has been shown that simulation of field evaporation [26, 27] can be performed with good agreement between experimental observation and simulation. This method has the benefit of being able to provide shapes at any point in the evaporation sequence without having to perform other microscopies. Given a good transmission (tomographic) image of the specimen, as

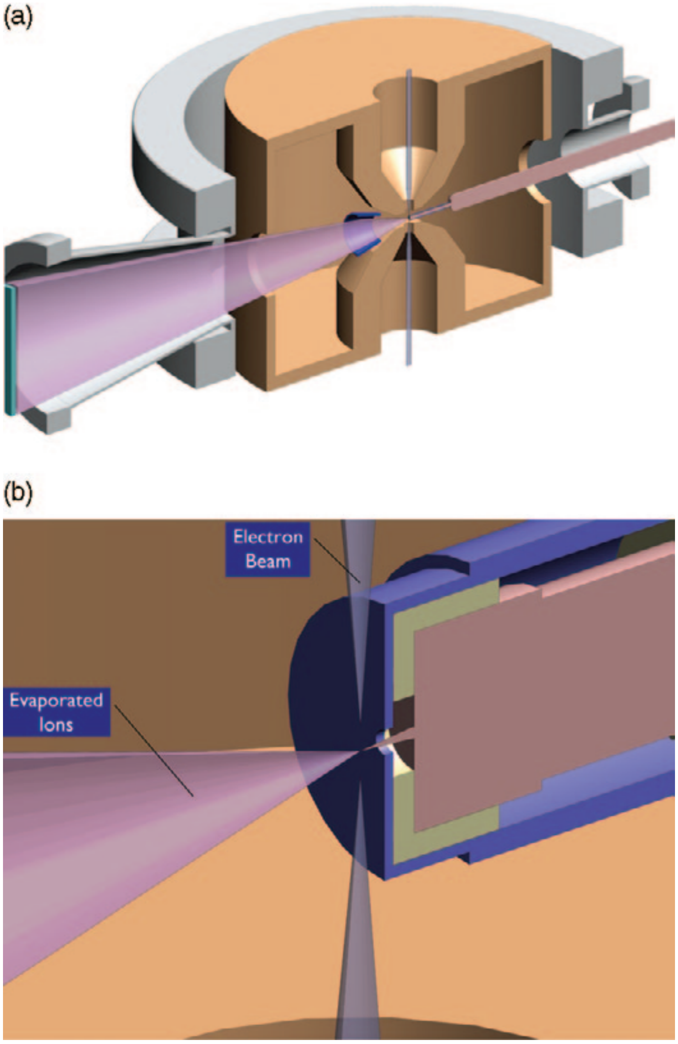

Figure 4: (a) Schematic illustration of the objective lens section of the proposed *atomscope*. The ion beam path is shown in purple diverging to the left and impinging on a position-sensitive detector. An ion optic that decreases the ion beam divergence is shown in dark blue. (b) Close-up of the specimen area in the *atomscope*.

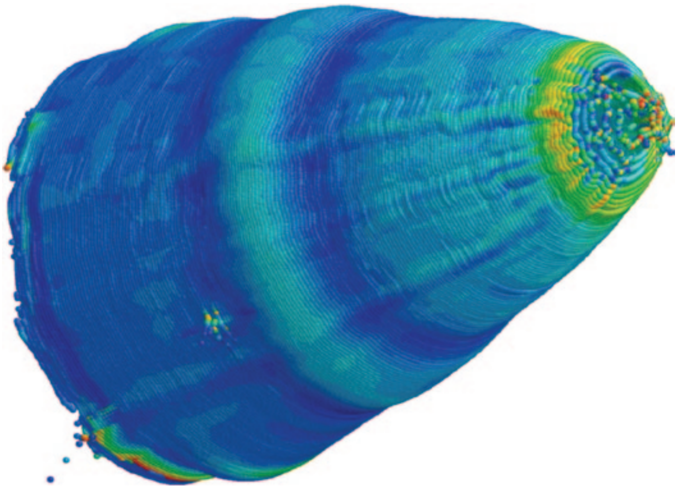

Figure 5: STA point cloud showing the mean curvature (false color scale) of the tip at every point on the missing-wedge-filled surface. The tip apex shape is readily apparent.

Table 1: Assessment of the contributions of TEM/STEM and APT to AST. Green text means the aspect is satisfied. Red text means the aspect is not satisfied.

Attribute	TEM/STEM	APT	APT + TEM/STEM
Spatial Fidelity (AST)	High	No (needs correlative information)	Yes
100% of atoms known (AST)	No	Potential for 100%	Yes
Discrete 3D image for a large volume (AST)	No (tomographic images)	Yes	Yes
Atomic and/or Crystallographic Structure (AST)	Yes (diffraction, phase contrast images)	Maybe (spatial distribution maps)	Yes
Microstructural Imaging: 2D	Yes	Yes	Yes
Microstructural Imaging: 3D	Yes (electron tomography)	Yes	Yes
Compositional Mapping: 2D	Yes (EELS, EDX)	Yes	Yes
Compositional Mapping: 3D	No	Yes	Yes
Chemical Mapping	Yes (EELS)	No	Yes
High Analytical Sensitivity	No	Yes	Yes

in Figure 5, for the starting point, the specimen model may be of very high quality. Here too, iteration of this process may lead to near-perfect reconstruction.

Structure-Properties Microscopy

The structural, chemical, and basic-properties data to be generated by the *atomscope* will provide precisely the data needed for integrated computational materials engineering (ICME). For the first time, direct experimental results may be incorporated in, for example, molecular dynamics simulations. This convergence between experimentally derived insights and modeling will provide unprecedented opportunities to advance fundamental knowledge of condensed matter physics and materials science.

Conclusions

Atomic-scale tomography is defined to be the ultimate microscopy. The prospects for achieving AST are examined here, and we find that there are multiple approaches that might reach this goal. Experimental programs should be initiated that seek to achieve 100% ion detection efficiency and perfection in the reconstruction process. Achieving AST is expected to have profound implications for materials science and engineering.

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