Advanced Characterization of Materials using Atom Probe Tomography

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Introduction:

Electronic device failures are influenced by numerous factors, including the choice of material and associated processing methods, as well as the service conditions the device will see, *e.g.*, temperature excursion, electric current, mechanical or thermal stress, cyclic or static electric fields, etc. The fundamental factors that influence failure modes come down to the interplay between atoms within the material. Among the analytical techniques that provide sub-nm spatially resolved chemical information, atom probe tomography (APT) has emerged as the best compromise between analytical sensitivity and spatial resolution, as compared to other analytical methods such as secondary ion mass spectrometry (SIMS) and transmission electron microscopy (TEM). Owing to the single atom specificity, APT can provide 3D chemical maps, or tomograms, of samples comprising any element or isotope in the periodic table, with sub-nm spatial resolution in three dimensions.

The ability to provide 3D reconstructions with sub-nm spatial resolution, and elemental specificity in the ppm range in some cases, has proven useful for diverse applications. To date, APT has been utilized for compositional profiling of geological minerals,[1] the direct observation of H poisoning at grain boundaries in steel,[2] cryogenically frozen biomaterial analyses,[3] and elucidating the atomic scale structure and composition of electronic materials and devices,[4] to name a few.

Atom probe tomography is an evolution of field ion microscopy, which provided the first direct glimpse of atoms in 1955, but at the time worked exclusively on metals.[5] The first atom probe microscope followed in 1967 and has been iteratively improved by many groups since then, with improvements in spatial resolution, mass resolving power, and analytical sensitivity, as well as the variety of materials that can be analyzed through the addition of 3D detectors, energy compensating optics, local electrodes, and advances in pulsed laser technology.

APT will be briefly reviewed here, focusing on the capabilities and advances to assist in the characterization of electronic devices. New materials integration and improved design can be promoted by using atom probe tomography as an analysis technique, shown through the following diverse examples in this article.

Experimental Overview:

The sub-nm spatial resolution and analytical sensitivity of APT is obtained through a process known as field ion evaporation. Field evaporation requires applying a high standing voltage (1 kV to 10 kV) to a needle-shaped sample, typically of diameter less than 100 nm at the apex. To encourage field ion evaporation, an additional external short high-voltage or laser pulse is used to emit the atoms already

under the applied field.[6]–[8] The externally triggered pulse is used to selectively evaporate surface material from the tip on an atom-by-atom basis. By removing single layers of a sample, ideally one atom at a time, and collecting the evaporated ions on a position-sensitive time-of-flight (TOF) detector (Fig. 1), a mass spectrum of each pulsed event can be obtained, and the x,y coordinates where each ion was intercepted by the detector are recorded. Current APT instruments have both straight flight path and reflectron configurations, with the latter employing electrostatic lenses to increase the mass resolution. The averaged TOF mass spectrum and the ion coordinate information are used to create a 3D virtual "model", with each voxel representing a sub-nm spatially resolved element (or isotope) from the original specimen.

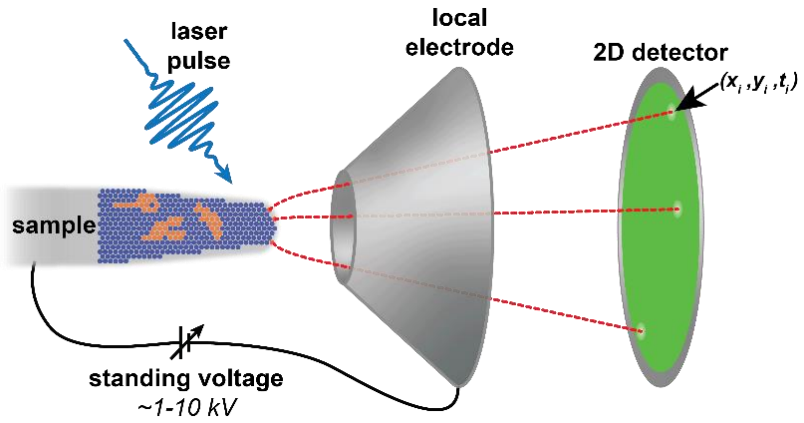

Fig. 1: A schematic showing the incoming laser pulse to a sample tip, resulting in field evaporation followed by ion detection on a 2D detector, adapted from [9].

APT is based on a thermal process that follows an Arrhenius rate equation (Eq. 1). The rate of evaporation (k) is increased by either decreasing the potential energy barrier (Ea) of atoms on the surface by increasing the applied field using a voltage pulse, or by increasing the temperature (T) of the material using a thermal laser pulse.

$$k = Ae^{-\frac{E_a}{k_B T}} \qquad \text{Eq. 1}$$

Cryogenic temperatures are used to suppress element diffusion on the surface of the specimen needle and confine the evaporation event to coordinate with the trigger pulse, thus increasing the signal-to-noise ratio. To that end, APT samples are mounted on a specimen stage that is cryogenically cooled to temperatures as low as ~20 K using liquid He.

Atom Probe Sample Preparation:

To obtain the high field required to ideally liberate an individual atom from the specimen surface, needle-shaped samples are employed. The required fields of 10 V/nm-50 V/nm can be obtained by applying a 5 kV standing voltage, for example, to a 100 nm diameter (or less) needle-shaped specimen. To prepare APT specimens with such geometry, a focused ion beam (FIB) lift-out method is often used.[10] Fig. 2 shows an example of APT tip preparation from a bulk substrate using this approach. First, the area of interest is identified, and a wedge is cut in the bulk material (Fig. 2a). The wedge is lifted out and a small section is welded to the tip of a sacrificial post (Fig. 2b) that is typically made from

W, Si, or a TEM grid bar.[11] The sample welded to the post is then sculpted to the final needle-shaped geometry using the Ga^+ ion beam and an annular milling scheme (Fig. 2c-e). Due to the numerous milling and imaging steps, a protective metal cap (often Ni, Cr, or FIB-deposited Pt) can be deposited first, over the sample surface to prevent Ga^+ ion implantation in the top layers.

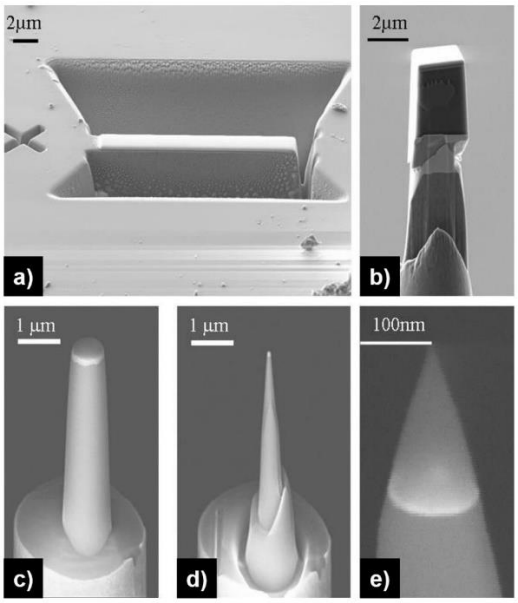

Fig. 2: A summary of APT tip preparation from a bulk sample showing the a) FIB-prepared sample bar, b) welded section transferred to an external post, and c-e) the gradual sharpening of the sample tip by annular milling. Adapted from [11] and reprinted under the terms of the Creative Commons Attribution License.

FIB-SEM methods also enable precise identification and extraction of site-specific specimens often localized within regions of several nm or less. In this way, nm-scale devices, defects, structures, or interfaces can be selected for APT examination.

Scope of Material Characterization:

APT is an experimental technique that provides sub-nm 3D maps of any element in complex material structures with analytical sensitivity approaching the ppm range. By evaporating single atomic layers of a sample atom-by-atom, followed by elemental identification in the mass spectra, the specimen can be virtually "reconstructed" to reveal many microstructural and chemical features relevant to device performance and failure. For example, APT can be used to show evidence of nucleation and clustering, segregation or depletion of species at grain boundaries, and other defects such as dislocations as long as they have an associated chemical marker like a Cottrell atmosphere or segregation of an element to a dislocation core. Additionally, APT can be used to measure chemical composition, oxygen stoichiometry, and spatially resolved dopant concentrations in 3D. It excels at measuring chemical gradients across buried, arbitrarily shaped interfaces, such as those encountered in patterned nanoscale heterostructure devices.

Measuring the chemical composition, uniformity, and 3D distributions of dopants and additives is extremely important to the function of nanoscale semiconductor materials, requiring high analytical and spatial resolution of each element in the device. To that end numerous electronic materials and devices

have been examined by APT, including various field-effect transistor geometries, magnetic tunnel junctions, photovoltaics, battery materials, ferroelectrics, thermoelectrics, light emitting diodes, and more. Such devices contain materials as varied as metals, oxides, semiconductors, silicides, nitrides, and even 2D materials. Several examples of APT applied to the above-mentioned applications are presented below.

Composition Analysis:

Composition analysis is important for devices that rely on precise control of the stoichiometry of chemical phases, for example, in InGaN-based light emitting diodes and quantum wells. Understanding the composition and uniformity of each layer is required to verify that the apparatus will perform the required function. As such, in an APT experiment, the composition of individual nanolayers can be determined and compared with other layers in the device. Fig. 3 shows a bulk InGaN quantum well structure (Fig. 3a). The inset dashed line indicates the ROI from which the APT tip was extracted. Here, laser-pulsed APT was used to determine the composition of each layer. The colorized 3D reconstruction (Fig. 3b), and mass spectra (Fig 3c.) from the various layers demonstrate the spatial resolution of the technique and how the composition varies in the different layers [12].

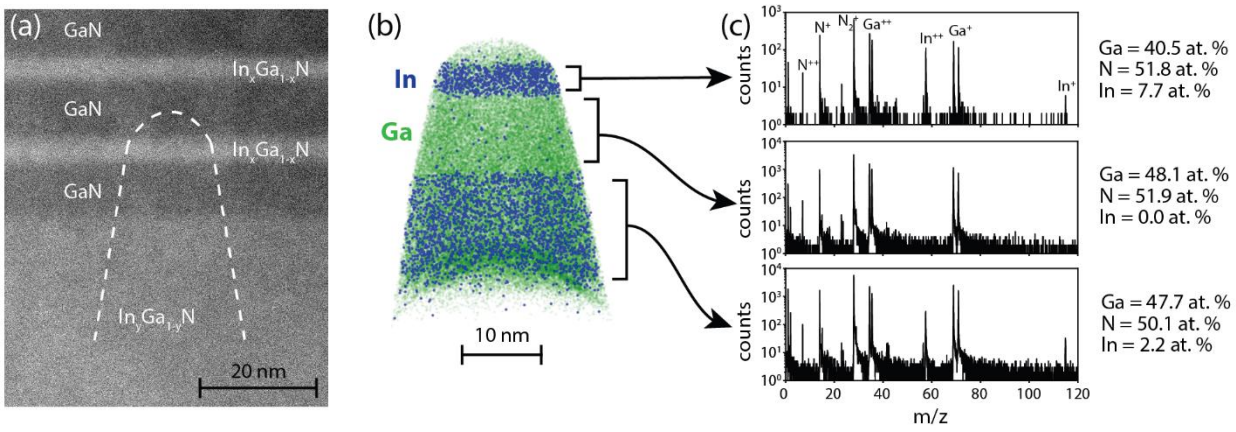

Fig. 3: a) A TEM image of the InGaN material cross-section with the APT tip area shown and nominal bulk layer composition, b) the APT reconstruction showing the separate material layers and c) the separate mass spectra and composition as measured by APT from each isolated layer.

As seen in Fig. 3, the quantity and dispersion of indium in each layer can be accurately determined after reconstructing the sample tip, showing the ability of APT to verify the device properties and dispersion of elements in the quantum well.

Interface Analysis:

Within a materials' microstructure, grain boundaries are critical to the overall bulk mechanical properties. For example, elements within a bulk material may segregate or deplete at grain boundaries during the fabrication process, causing undesirable effects such as embrittlement. APT can be used to provide 1D composition profiles (the areal average along one dimension) and 3D chemical maps of samples containing multiple layers, thereby resolving the composition and location of different elements segregated to interfaces or grain boundaries due to processing. Fig. 4 shows an example of a high-

entropy $Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}$ alloy in which ductility measurements recorded as a function of temperature suggested that grain boundary embrittlement was the reason for crack initiation.[13] To gain further insight into the embrittlement, an APT sample was extracted from a grain boundary in the alloy (Fig. 4a). The 3D tip reconstruction results revealed Cr-, Mn-, and Ni-rich regions at the grain boundary (Fig 4c-d), and 1D composition profiles along different lines showed concentrations of these elements was up to 10 at. % greater than in the bulk. This fast nanosegregation during tensile testing at elevated temperatures reduces grain boundary cohesion and leads to embrittlement and grain boundary cracking. In the APT reconstruction, complex grain boundaries and the distribution of elements or clusters can be visualized.

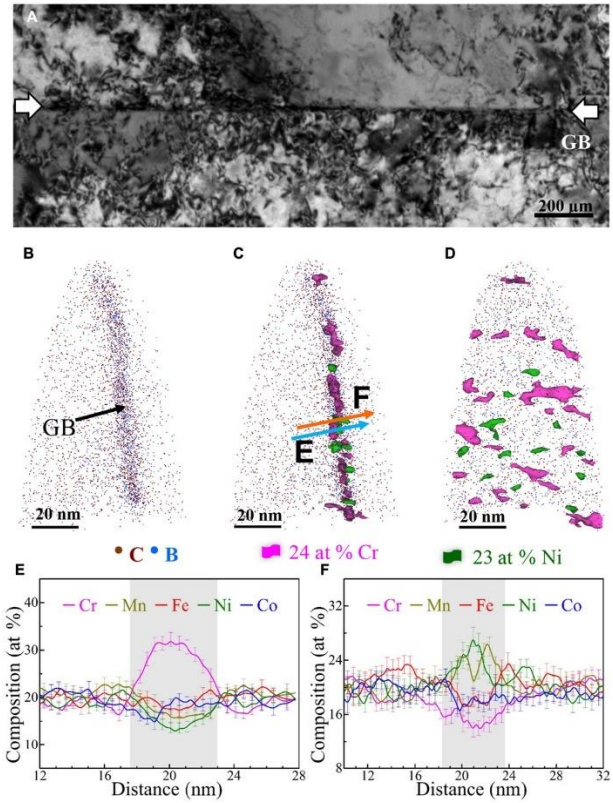

Fig. 4: Example of segregation to grain boundaries and cluster identification. a) TEM image of the alloy sample, b) APT reconstruction “atom map” of the sample tip showing grain boundary segregation of Cr and Ni, c) side (cross-section) view of the grain boundary with isoconcentration surfaces delineating areas of 23 at. % Ni and 24 at. % Cr enrichment, d) plan view (looking perpendicular to the grain boundary), e) 1D composition along arrow “E” and f) 1D composition along arrow “F” in section C. Reprinted from [13] under the terms of the Creative Commons Attribution License.

Site-specific specimen preparation has been used to access discrete nanoscale devices including p- and n-type MOSFETs, gate stacks and FinFET structures for APT analysis.[14]–[16] In one example,[14] alloying elements and dopants, such as Pt or As, are commonly present in the region near silicide contacts in an n-type MOSFET, but the exact role of stress and defects on the redistribution of those species upon annealing is still a topic of debate. In Fig. 5a, the 3D APT reconstruction shows the separate layers of the NiSi contact, poly-Si gate, and the SiO_x spacers. The authors find notable clusters of platinum arsenide in the NiSi phase and inhomogeneous segregation to interfaces (not shown).

However, 1D top-down composition profiles through a central 10 nm diameter cylindrical region either through a patterned device (Fig. 5b) or on an unpatterned blanket wafer (Fig. 5c) reveal little difference between the Pt and As distributions. Such results, according to the authors, indicate the total silicide process, rather than spatial confinement in the patterned device, controls element distributions upon annealing in these structures.[14]

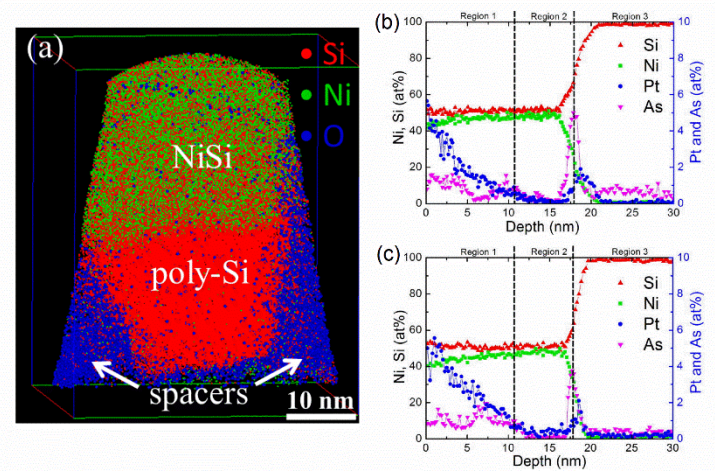

Fig. 5: a) An APT reconstruction of a poly-Si MOSFET device, b) a 1D top-down composition profile through the device layers and c) a 1D top-down composition profile of an unpatterned test zone from a blanket wafer subjected to the same silicide process as b). Adapted with permission from [14].

Thermally grown interfacial layers, dopant diffusion, interfacial characterization, and the separate processes leading to element segregation in the material can be analyzed with higher accuracy using APT than other methods in this context, meaning that important conclusions can be drawn from experiments such as these, which ultimately leads to improved device function.

Elemental Clustering and Proximity Histograms:

APT can also offer insight into the size and composition of extremely small clusters hidden within layers of a material or device. Fig. 6 shows an example of GeTe-based thermoelectric device analysis using APT, with the authors ultimately linking Ga-rich cluster formation to changes in the electron and phonon transport.[15] The authors produced a sandwiched Ga_2Te_3 sample (Fig. 6b) and after APT analysis, separate atom maps for the elements present in the GeTe section of the tip (Fig. 6a) reveal Ga-rich clusters. APT analysis also offers the ability to integrate concentrations across arbitrarily shaped 2D interfaces defined by a particular element or molecular concentration to create what is called a proximity histogram. Here, a single Ga cluster was selected in the APT reconstruction, visualized to show the cluster size (Fig. 6c), and a proximity histogram of the cluster was used to show an increase of Ga concentration over the surrounding area (Fig. 6d). Ultimately, APT can show complex 3D structures with accurate composition analysis that can tie back to the overall device performance.

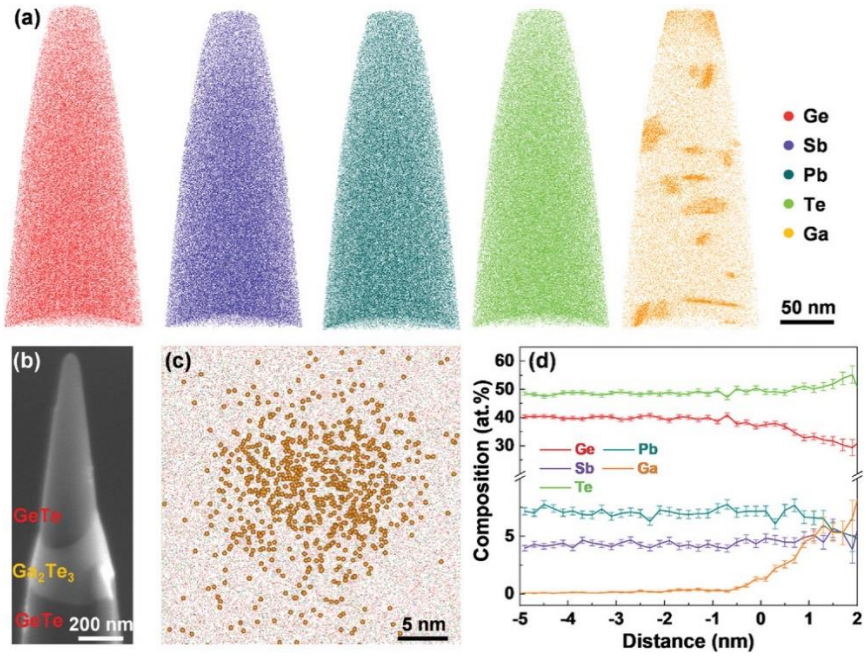

Fig. 6: APT reconstruction data of a GeTe sample showing a) separate ion distributions in the reconstructed APT tip, b) scanning electron microscope image of the tip, c) 3D distribution of a selected Ga cluster in the APT data and d) proximity histogram calculated by integrating the composition from a 1.5 at. % Ga isoconcentration surface (x = 0 nm, not shown) around the Ga-rich cluster, showing changes in composition upon crossing the cluster surface. Reprinted from [15] under the terms of the Creative Commons Attribution License.

Outlook:

Recent advances involving shorter wavelength light sources have resulted in improved analysis of a broad range of materials that have historically been difficult to measure with conventional near-UV APT methods, such as wide-bandgap insulators. Commercial systems are now utilizing wavelengths in the deep-UV region of ~257 nm, while NIST has pushed into the extreme-UV at ~27.5 nm.[9],[16] A shorter wavelength (higher photon energy) may improve the evaporation yield of certain materials by utilizing increased absorption cross-sections and higher photon energies. However, experiments in this regime are sparse, with the benefits and drawbacks not yet fully determined. Concurrently, cryogenic techniques have been implemented, enabling the probing of organic and biological samples.[3], [17], [18] Although organic materials are typically difficult to accurately analyze, capabilities resulting from the above improvements can be exemplified in the analysis of an organic marine protozoan material (Fig. 7), showing Na ion segregation between the carbonate skeleton and primary organic sheet.[19] The Ca interface is highlighted (Fig. 7a) and the segregation of the Na ions is shown in the APT reconstruction (Fig. 7b). The composition around the phase boundary can be determined from APT data in the form of a proximity histogram, giving changes in the concentration profiles of specific elements on either side of the complex structure (Fig. 7c-d). The segregation of Na and Mg ions provides insight into the carbonate nucleation process, supplying new information of diverse carbon-based samples by APT and demonstrating a higher need for ion-specific investigation of biomineralization.

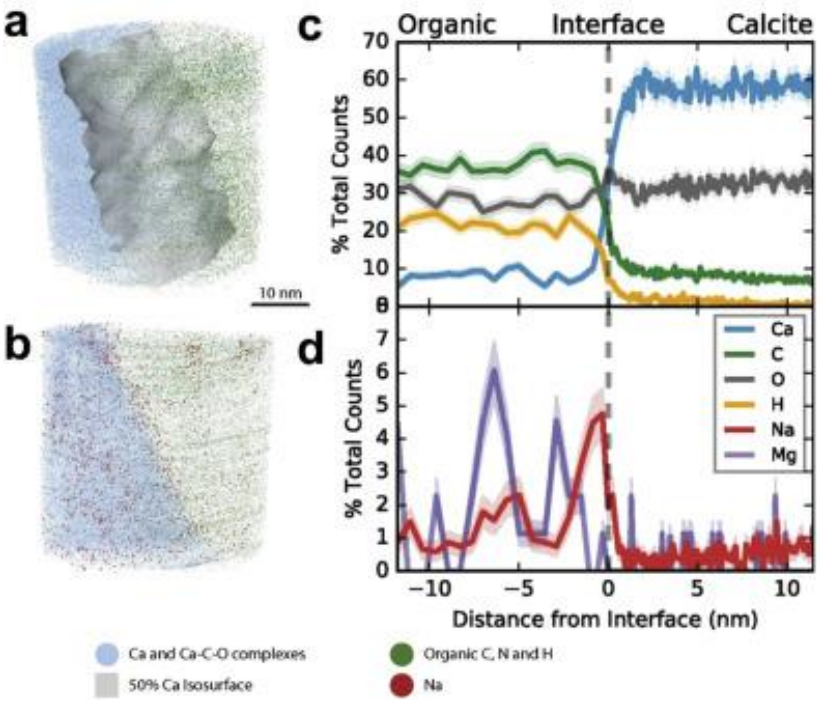

Fig. 7: APT analysis of a marine protozoan showing a) the organic/calcite interface delineated with a 50 at. % Ca isoconcentration surface, b) Na ion (red) distribution, and c-d) composition proximity histograms across the calcite interface in a). Adapted from [3] under the terms of the Creative Commons Attribution License.

Despite the numerous progressions in application, APT experiments still have several challenges to overcome. Due to the high applied field, samples are often under high electrostatic stress, which can result in unexpected sample fracture during data collection. If the sample survives through the entirety of the data collection without fracture, the subsequent analysis and reconstruction of the data may be less than trivial, often requiring correlative microscopy techniques to ensure spatial fidelity with the original specimen. In Si-based FinFETs, for example, the varied materials and accompanying thermal and absorption properties in a single device can lead to errors in the reconstructed shape or appear to show unrealistic mixing of layers,[20] requiring careful consideration to produce accurate 3D representations. Nevertheless, computational and experimental techniques continue to improve, offering valuable insights to the compositional microstructure of materials and increasing the likelihood of successful sample analysis.

A brief review of APT and the capabilities of this instrumental technique were discussed here, touching on some of the history and research within the field. For additional review articles and information, readers are directed to previous articles.[4], [21], [22] Although there is a wide range of material experiments and theoretical exploration that was not discussed, the utility of ATP continues to grow. Electronics, semiconductors, and interface analysis will benefit from more accurate characterization with better spatial resolution as APT-based techniques are improved, leading to devices and materials of unparalleled performance and reliability.

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