Atom Probe Tomography 2012

Thomas F. Kelly and David J. Larson

CAMECA Instruments, Inc., Madison, Wisconsin 53711; email: thomas.kelly@ametek.com, david.larson@ametek.com

Abstract

In the world of tomographic imaging, atom probe tomography (APT) occupies the high-spatial-resolution end of the spectrum. It is highly complementary to electron tomography and is applicable to a wide range of materials. The current state of APT is reviewed. Emphasis is placed on applications and data analysis as they apply to many fields of research and development including metals, semiconductors, ceramics, and organic materials. We also provide a brief review of the history and the instrumentation associated with APT and an assessment of the existing challenges in the field.

Keywords

local electrode atom probe, atomic-scale analysis, LEAP, APT
INTRODUCTION

If the purpose of tomography is to obtain a three-dimensional view of the internal structure of an object, then atom probe tomography (APT) sits alone at the high-resolution end of spatial scales as the analytical technique with the highest spatial resolution. If every atom were identified and positioned in a volume, then APT may be called the ultimate tomography. The technique cannot yet perform the latter, but it is close to doing so, and there are plans to achieve to this goal (1–3). In the meantime, the technique offers analysts the opportunity to examine inorganic and organic materials with a three-dimensional image made up of detected atoms or small molecules (up to 60% detection efficiency) with high spatial resolution (better than 0.3 nm achievable in all directions) and high analytical sensitivity (as good as 1 appm) over volumes of greater than $10^6$ nm$^3$ (100 nm \times 100 nm \times 100 nm). These attributes are a powerful combination.

As with any analytical technique, APT has limitations. Most notably, not all specimens will run successfully, and for some complex material structures, the reconstruction of the three-dimensional image can have severe distortions (4, 5). For those structures that do not have these problems, the results can be awe inspiring. The examples chosen for this review provide a good sampling of the kinds of successes the technique has achieved.

History of Atom Probe Tomography

The history of APT is one of successive invention by an individual, Erwin W. Müller. In 1935, he invented the field emission electron microscope (6), which was further adapted into the field ion microscope (7), which in 1955 produced the first human-generated images of atoms (8, 9). By 1967, to identify those atoms, Müller and coworkers (10) had invented the atom probe field ion microscope, which has undergone numerous major improvements, including the imaging atom probe in 1973 (11) and the position-sensitive atom probe in 1988 (12). The current most common geometry is a local electrode atom probe (LEAP) (13), which first appeared commercially in 2002. This instrument has a focused small-spot laser beam (14) that first appeared commercially in 2005 with a 10-μm-diameter beam and is now in its second generation with a <3-μm-diameter beam. There are also many remote-electrode instruments (15, 16) and a microelectrode geometry (17), each using large-spot (>50-μm-diameter) laser beams. Historical summaries of the field can be found in Miller et al. (18) and Miller (19). Kelly & Miller (20) provided a summary of the hardware configurations, and Kelly & Larson (21) recently published a more recent and personalized history of the development of the LEAP.

Current Activity

With the introduction of the LEAP and other commercial non-LEAP configurations in the past decade (15, 22), major progress has been made for hardware configurations so that present-day commercial atom probes have become practical instruments. There have been major increases in data-collection rates of four orders of magnitude (to $5 \times 10^6$ atoms min$^{-1}$), in field of view of two orders of magnitude (to $3 \times 10^3$ nm$^2$), and in mass-resolving power (MRP) of an order of magnitude (to >1,500) since 2000. These hardware and software developments have led to a burgeoning of applications as described below. By various estimates, the number of people actively using atom probes has quadrupled in the past decade. Perhaps most importantly, the number of atom probes being used for industrial research and development has increased by an order of magnitude in that same time. This latter trend is taken as a sign that the technique is achieving the maturity needed for commercial adoption. Much improvement remains to be realized, but the technique is providing information of real value to both academic and commercial users.
These performance improvements are crucial, but the introduction of reliable laser pulsing remains the single most important development impacting applications development (22–24). Because APT is based on time-of-flight spectroscopy, the evaporation rate must be pulsed to know the start time of the evaporated ion. For the first 35 years of atom probe’s history, metals were studied almost exclusively because the technique required that specimens have high electrical conductivity to accomplish electric field pulsing of the evaporation rate. Laser thermal pulsing of the evaporation rate enabled exploration of atom probe applications from the entire spectrum of condensed matter materials regardless of their electrical behavior. As a result, researchers are developing applications using semiconductor materials of all kinds, ceramic materials, and organic and biological materials. Second-generation laser systems that employ UV photons have now been developed (25), which offer greater performance and specimen yield.

THE STATE OF INSTRUMENTATION

Fundamental Considerations for Design of Instrumentation

Atom probe instrumentation experienced a phase of rapid development in the first decade of the 2000s [see Kelly & Larson (26) for a brief history]. These tremendous gains in performance of APT instruments (15, 25, 27, 28) give cause to consider the extent to which better performance can be achieved. Greater MRP is desirable, but not at the cost of field of view: When MRP is sufficient for a task, then field of view is more important. The converse is also typically true. The challenge for instrument design is to find the optimal trade-off. In Figure 1, a straight-flight-path atom probe geometry is illustrated. When the flight path length, $L$, is small, the detector subtends a large solid angle in the data path, which produces a large field of view, $\phi$. The flight times are small when the flight path length is small, so high repetition rates may be used. However, the timing uncertainty will be a finite number, and for small flight times, it can lead to unacceptable uncertainties in the timing resolution or resultant mass resolution for ions. If the energy spread for similar ions is negligible, the timing uncertainty does not change during flight, so if the flight path length is increased, the relative timing resolution will improve, and greater flight path lengths can produce higher mass resolution. There is generally thus an inverse relationship between field of view and MRP. The challenge is to push this envelope of MRP and field of view to greater values.

In laser pulsing of atom probes, the energy spread for many materials is almost negligible, $\lesssim 3$ eV, which makes it possible to achieve high MRP with long flight times. However, some materials may have a large intrinsic energy spread ($\sim 20$ eV) in laser pulsing that is large enough to defeat the goal of achieving high MRP with long flight paths. The source of this large energy spread has not been identified, but fortunately it appears that few materials have a large energy spread in laser pulsing. When long flight times lead to high MRP, optical elements may be used to bend the ions back toward the central axis to recover field of view for a given $L$, as shown in Figure 1. This concept was first developed for a three-dimensional atom probe by Bostel et al. (27, 28) and was commercialized by Cameca.

Reflectron-Based Instruments

Given that energy spread may be greater than a few electron volts even in laser pulsing, the options for improving peak discrimination are energy compensation or energy determination. Energy compensation seeks to equalize ion flight time by causing ions of higher energy to take longer pathways to the detector. When done correctly, all ions of a given mass-to-charge-state ratio have the same flight time. These systems make it possible to achieve high MRP in voltage-pulsing mode as well as in laser-pulsing mode even when large energy spreads exist.
Figure 1
Geometry of a typical atom probe. $V_{tot}$ is the total accelerating voltage of the system. $V_{ext}$ is an extraction voltage used with both static and dynamic fields. $V_{pa}$ is a postacceleration voltage that can range in value from zero to magnitudes comparable to $V_{ext}$. $V_{p}$ is a voltage pulse that is the time-varying component of dynamic fields. $L$ is the flight path length to the center of the detector, and $R$ is the radius of the detector.

Manyrin et al. (29) designed the first reflectrons for general mass spectrometry. Waugh et al. (30) first used reflectrons in APT for one-dimensional atom probe instruments. Cerezo et al. (31) adapted reflectrons to an imaging application in three-dimensional atom probes within a few years. All these reflectrons used planar electric fields, which became a problem in imaging instruments because, although they create an output surface with reduced timing spread, this comes at a cost of introducing spatial aberrations for ions of different energy. The field of view was therefore restricted to small values ($\sim 15$ nm diameter) to limit this effect. Panayi (32) solved this problem by designing a curved reflectron in which the output surfaces for time-focused ions and spatial-focused ions are made to nearly coincide. As a result, the field of view of curved reflectrons can be made an order of magnitude larger ($>150$ nm diameter). These curved reflectrons were adapted to a commercial remote-electrode atom probe (22) and are currently used in one model of LEAP instrument.

THE STATE OF SPECIMEN PREPARATION

Automated Electropolishing Instruments

Today, atom probe specimens consist of a sharp needle with an apex radius measuring 20 to 200 nm and a modest shank angle ($\lesssim 10^\circ$ semiangle). The small specimen size enables the high ($\sim 10–50$ V nm$^{-1}$) electric field necessary for field evaporation. Because the needle-shaped specimen is the primary optic of the microscope, specimen preparation forms a critical step in a successful APT analysis.
Historically, needle-shaped specimens formed by electropolishing were the norm for APT. Standard techniques have been applied primarily, although not exclusively, to metals since the inception of high-field work in the 1930s. General information on the techniques can be found in References 33 and 34, and a veritable bible of electropolishing and chemical polishing solutions may be found in section 9 of Reference 35. In addition to the standard manual techniques, automated apparatuses have emerged commercially (36). Simplex Scientific (Middleton, Wisconsin) offers an instrument called the electropointer that automatically prepares needle-shaped specimens. Once the starting wire or piece is inserted into the apparatus, the instrument automatically controls the voltage and current applied to a small wire loop surrounding the specimen normal to its long axis. The loop is moved longitudinally by stepper motor. All motions and electrical signals are controlled and monitored by a computer. There is also an integrated high-magnification light optical microscope that displays the specimen during operation. With this instrument, a blank specimen is inserted, and a specimen that is ready for atom probe analysis is output without the need to verify its sharpness.

Focused Ion Beam–Based Preparation

The criteria for most specimens prepared for APT analyses are fundamentally the same. (a) The specimen must be sharp enough to produce field evaporation. (b) The specimen must be robust enough mechanically to allow for significant evaporation to occur. (c) The feature of interest to the user must also be present in the near-apex region to ensure that the feature is included in the evaporated data.

Using ions to assist in the preparation of specimens for field ion microscopy or APT dates back nearly 40 years (37). Several researchers have used broad ion beams (38–43) to assist in specimen preparation, and early efforts included using focused ion beams (FIB) (44, 45), although the degree of focusing in these early instruments was not high. The advent of the current generation of FIB instruments in the 1990s began a revolution in preparation methodology for APT. The ability to image specimens (using ions in and secondary or backscattered electrons out) coupled with the ability to remove substantial amounts of materials using ions enabled the ability to see the features of interest in specimens at high magnification while they were being sharpened. Over the past decade or so, this new capability has totally changed the types of studies to which APT may be successfully applied.

The earliest FIB-based methods to sharpen specimens for APT relied on attaching a volume of material to the end of a needle (43, 46) (using non-FIB methods) and shaping the end-form for APT analysis with FIB (47–50). Optimal annular milling methods that provided for improved emitter shapes were gradually developed (51–55). These methods allow the user to see the majority of the specimen apex volume during preparation and are generally applicable to most materials. If care is taken during the final steps of preparation, minimal ion-induced damage will be present in the specimen region of interest (56). APT lift-out methods (55, 57–60) were adapted from transmission electron microscopy (TEM) techniques (61). Using these methods, researchers may remove a small region of material from nearly any structure while they view it in the FIB. This small region of material eventually forms the apex region of the specimen. Details of these methods are described below.

The specimen-preparation landscape again changed significantly after Nishikawa developed the scanning atom probe (62), enabling the local electrode instruments that followed (13, 63, 64). With the electric-field-defining elements of instruments confined locally near the specimen apex (e.g., within less than ~50 μm), specimen geometries were no longer constrained to needles. For example, investigators developed microtip-array carrier tips (60, 65) that can be used in a FIB...
to make large numbers of specimens at one sitting with reproducible conditions. This leads to reproducible specimen geometries and greatly improves experimental repeatability.

Today, many applications and variations of the standard lift-out and sharpening methods have been reported (55, 66–73). These include variations enabling analysis parallel to the original specimen surface (“cross-section” orientation) (74) or inverted relative to the original specimen surface (“backside” orientation) (75, 76).

Site-Specific Specimen Preparation

For many applications, FIB-based site-specific specimen preparation is required. The general steps used in this preparation applied to the case of a FinFET (77) are illustrated and further described in Figures 2 and 3. Some preparatory preprocessing or deprocessing of the device structure may be necessary prior to lift-out (Figure 2) and sharpening (Figure 3). Preprocessing often includes applying a protective sacrificial cap to the top surface (71).

THE STATE OF APPLICATIONS

Introduction

Applications of APT have expanded rapidly over the past decade. The availability of high-quality commercial instruments has pushed the performance and reliability of atom probes, greatly

Figure 2

The steps involved in a standard focused ion beam (FIB) lift-out procedure. (a) A FIB-deposited protective strip is placed over the region of interest. This protective material is often Pt or W. (b) The material is then removed by ion milling around three sides of the region (arrows) as well as underneath to produce a long cantilevered wedge of material. (c) The wedge is removed by using an in situ micromanipulator (attached to the left end of the wedge) and then cutting the wedge free from the substrate (vertical white line). (d) The micromanipulator is used to position the wedge above the carrier microtip (seen in plan view). (e) The wedge is attached to the carrier-tip surface with FIB-deposited Pt (arrow) and then cut free from the carrier tip (vertical white line) for transfer to additional microtips. Once propagation of the wedge is complete, the FIB stage is rotated 180° so that a second Pt braze can be applied to the opposite wedge-post interface of each mounted post. (f) The final mounted wedge section is then ready for sharpening: The line of the targeted FinFET is clearly visible along the line of the arrows.
Figure 3
The steps involved in the focused ion beam (FIB)-sharpening process converting the wedge section in Figure 2 into a specimen for APT analysis. (a) The region of interest is shown by the arrow. (b) The first annular milling pattern shapes the tip into a cylinder, with the FinFET region clearly visible near the upper-center portion of the cylinder. The second and third milling patterns produce (c) a tapered end and (d) a narrowed end. The final sharpening step is performed at low ion energy (either 2 keV or 5 keV) and is simply a circular pattern that images the specimen end-on (56). During this stage, the specimen is carefully monitored to ensure that the region of interest is positioned near the apex of the final specimen. (e,f) The low- and high-magnification images of the specimen that is then ready for APT.

impacting the breadth of available applications. However, the most significant factor in expanding the universe of applications is the renewed utilization of laser pulsing. This is true for materials that cannot be field evaporated successfully with voltage pulsing. Yet, laser pulsing is also beneficial for a range of metals applications for which premature specimen fracture is a problem. Certain metal specimens, including high-strength steels, for example, will not run with adequate yield with voltage pulsing because the stress in a specimen varies with the square of the applied electric field (78) and voltage pulsing uses higher electric fields than does laser pulsing. These specimens will often run with much higher success rates in laser pulsing.

Metals
Because the atom probe technique relied almost exclusively upon voltage pulsing in its first three decades, virtually all the work from the 1970s through 2000 was on metals. As a result, these applications tend to be the most mature. However, new and more sophisticated applications are constantly being pursued and reported in the literature. This section highlights three metals applications that illustrate the latest trends and the newest applications.

A trend in microscopy today is the correlative use of TEM and APT for materials studies at the atomic scale. The complementarity of these two techniques is particularly strong and is likely to lead to greater integration of the two techniques. Two examples are given here to illustrate the synergistic correlative opportunities that may be exploited with TEM and APT. Srinivasan et al. (79) used high-angle annular dark field STEM (scanning transmission electron microscopy) and APT to study the order-disorder transition between the disordered $\gamma$ matrix and ordered $\gamma'$ precipitates in a nickel-base superalloy (Figure 4). STEM was used to elicit the variation
Figure 4
Order-disorder transition at a heterointerface. (a) \{002\} plane intensity in high-angle annular dark field STEM (scanning transmission electron microscopy) at the γ-γ' interface. (b) Atom probe tomography (APT) image with γ phase (Co atoms shown in blue) and γ' phase (Al atoms shown in red). (c) Close-up of the lower interface in panel b showing the Al atoms in the \{002\}, where the interface transition based on atomic ordering is approximately 4–6 atomic layers (0.7–1.0 nm) thick. (d) A proximity histogram [or proxigram (160)] across the same interface showing a compositional interface width of approximately 2 nm. Reprinted with permission from Reference 79. Copyright 2009, American Physical Society.
in order across the coherent \{001\} heterointerface through intensity ratios of the aluminum-rich/aluminum-poor \{002\} plane signal. APT was used to measure the aluminum composition profile and to estimate the ordering transition width across this same interface type. The two techniques agree very well. Furthermore, the experimental results matched with high precision the atomistic modeling results of Mishin (80) and Ardell & Ozolins (81). This experimental study (79) found that the order-disorder transition width is smaller than the compositional width of the interface, which raises fundamental questions concerning the definition of interface width at order-disorder interfaces. This work illustrates an important trend in APT work today: a strong convergence between the increasing capabilities of atomistic modeling and the experimental data available from APT (and TEM). This synergistic relationship is expected to continue as a natural marriage of atomic-scale predictive and characterization capabilities.

Gault et al. (82) studied an Al-Cu-Li-Mg-Ag model alloy with TEM and APT to elucidate the structure and composition of precipitates in the material. Excellent correlation was found between the TEM and APT results, as illustrated in Figure 5. Note, for example, that the phase contrast in Figure 5a surrounding the plate-shaped \(\theta'\) phase suggests the presence of an ordered L1\(_2\) phase, which has been suspected to be \(\delta'\) (Al\(_3\)Li). The APT composition profile in Figure 5c shows a clear increase in Li concentration on the outer parts of this precipitate, which is consistent with the hypothesis of a \(\delta'\) wetting layer on the \(\theta'\) phase. In this example, each of the two techniques

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**Figure 5**

Numerous second-phase features are visible in both the high-resolution transmission electron microscopy image (a) and the atom probe tomography (APT) image (b), which are taken from different specimens. These include a plate-shaped \(\theta'\) phase (Al\(_2\)Cu) in the orange ellipse that is connected to a spheroidal Guinier-Preston-Bagariastkij (GPB) zone in the light blue circle, an isolated spheroidal GPB zone in the dark blue circle, and a lath of the S phase (Al\(_2\)CuMg) in the red ellipse. A composition profile from APT across the white arrow in panel a is shown in panel c, which reveals the presence of elevated concentrations of Li on the edges of the \(\theta'\) phase. Reprinted from Reference 82 with permission from Elsevier.
provides complementary information that is crucial to support the conclusion and that would not be available from a single instrument.

One of the great unresolved challenges for analytical microscopy has been the ability to map hydrogen quantitatively in materials on a submicrometer scale. APT has been long considered for this task, but questions concerning the origin of the hydrogen, whether it truly emanates from the specimen or is adsorbed from the vacuum system, need to be addressed. Furthermore, hydrogen is very mobile in most materials, which makes it difficult to analyze in thin APT specimens. Showing that hydrogen concentration varies with position in a microstructure in a way that correlates with expected behavior would lend credence to qualitative mapping. Furthermore, if a phase with known hydrogen concentration can be analyzed, then an assessment of the quantitative accuracy can be made.

There have been several efforts in the past three years to demonstrate the capability of APT to map hydrogen in materials (83–87). Takahashi et al. (86) used an environmental chamber attached to an atom probe to charge deuterium in steels at room temperature and to quickly get them to the cryogenic stage of the atom probe. They showed that deuterium is trapped at the interface of titanium carbides with the matrix. Sepehri-Amin et al. (88) analyzed NdH2 hydrides in an Fe-rich matrix from Nd-Fe-B powder particles (Figure 6) and found a hydride composition of 64 at% H and 33.1 at% Nd, in good agreement with the expected stoichiometry. Their success is likely due, in part, to the fact that hydrogen is not mobile in this compound.

Cryogenic specimen transport systems for atom probes have become available commercially in the past year from a collaboration between CAMECA and Leica. This development should enable better studies of materials such as steels in which hydrogen is mobile at room temperature and that therefore must be quenched and kept frozen after treatment with hydrogen.

**Silicon-Based Semiconductor Materials**

Characterization of semiconductor device features and defects over the past few decades has been achieved primarily through use of electron microscopy, ion microscopy, various X-ray technologies, and some light-optical techniques. As the industry has moved further into the nanoelectronics realm, the use of these methods has become more challenging owing to the scale and dimensionality of the devices of interest and limitations of what have become standard techniques within the industry. One significant goal in the application of APT to silicon-based structures has been the analysis of functional devices. Downscaling of devices and the reduction of source/drain junction depths to avoid short-channel effects, combined with the increased field of view now available in modern atom probes (13, 64), make analysis of entire device structures a reality. Several researchers have recently used APT in the analysis of portions of partially processed device structures as well as in analysis of entire devices (71, 72, 89–99); selected examples are reviewed in this section.

Inoue and coauthors (90–92, 99) recently conducted substantial investigations of the distribution of dopants in various parts of MOSFETs. Knowledge of the detailed dopant distributions in microelectronic devices is becoming increasingly important as the devices get smaller and move into three dimensions. Figure 7 provides details of the n- and p-MOSFET gate regions of a recent transistor structure.

Various authors have recently investigated FinFET-type devices using APT. FinFETs (77) are “fin”-based field-effect transistors that maximize the area of the gate oxide by wrapping the oxide and gate structure around a feature that resembles a fin (Figure 8a). Intel recently announced a plan to employ this technology in the near future for its 22-nm technology-node products (100). The International Technology Roadmap for Semiconductors refers to these types of structures, which are part of a larger group of devices called multigate transistors, as “advanced nonclassical
Figure 6
Analysis of hydrides in hydrogen-disproportionated Fe-Nd-B powder. (a) TEM image of an atom probe tomography specimen in which the brightly imaging phase is NdH2. (b) Atom maps for Nd and H showing the hydrides. The subvolume for atom maps in panel c is shown as the black box. (d) Composition profiles along the long axis of the subvolume in panel c. Reprinted from Reference 88 with permission from Elsevier.
Figure 7
MOSFET gate regions. (Left) In the n-MOSFET gate region, phosphorus atoms segregate at grain boundaries and polycrystalline silicon/oxide interfaces. (Right) In contrast, no segregation of boron atoms is observed in the p-MOSFET gate (99). Arsenic and boron atoms were detected in the source/drain regions and channel regions, respectively, for the p-type FET (and vice versa for the n-type structure). Statistical evaluation of the data suggested that the fabrication process increases the boron fluctuation but not the arsenic fluctuation, thus producing more variations from device to device in p-type MOSFETs (99) (figure courtesy K. Inoue, Kyoto University, Japan).

CMOS devices” (77). Gilbert et al. (95) also studied this structure (shown in Figure 8). They found significant segregation of boron at the TiN/Si interface at the top of the FIN, but not at the same interface on the device sidewalls. They also reported several observations of artifacts in the nature of the three-dimensional reconstruction of such structures, which highlights the need for improvements in this area (4, 5, 101).

In FINFETs, as in MOSFETs, device performance may be altered by an inhomogeneous distribution of dopants. Recently, Kambham et al. (94) analyzed the conformality of boron implantation as a function of implantation angle in FinFET-type structures. They found that, for the 45° implantation (measured between the plane of the wafer surface and incoming dopant trajectory), the vertical peak concentration is approximately two times the lateral-profile peak concentration. However, in an implantation done at 10°, the dopants were more shallow and reduced in concentration. Observations of high nonconformality of the dopants with the sidewall dose at only 10% of the top dose compare favorably with previous modeling results from Vandervorst et al. (102).

Although APT has been applied to transistor and FINFET-type structures as described above, these structures have often been stopped at some point in the fabrication process to accommodate the analysis. There are many situations in semiconductor processing in which APT analysis of a finished product is desirable; competitive analysis and failure analysis are two good examples. Only recently have APT results been obtained from fully processed “off-the-shelf” transistor structures that are part of a finished product (72, 96–99). Figure 9 presents data showing the feasibility of APT analysis for fully packaged integrated-circuit microelectronic devices.
Figure 8

(a) A schematic and (b) an atom probe tomography data reconstruction of an entire high-k metal gate FinFET structure (100 nm in height and 20 nm in width) starting with nickel silicide (near top) and ending near the bottom of the FIN (bottom) (figure courtesy M. Gilbert, IMEC).

The field of view of the atom probe for this device is adequate to observe portions of the source and drain on either side of the channel. In future technology nodes, the transistor characteristic lengths will be smaller, and the present field of view achieved in this work will cover a larger portion of the components outside the channel. Although atom probe analysis of packaged devices is not currently routine, we expect that this approach to specimen preparation and analysis will mature quickly.

**Compound Semiconductor Materials**

Researchers have achieved much success using gallium nitride (GaN) as the basis for a wide range of optoelectronic devices. Unintentionally doped GaN emits in the ultraviolet range, and alloying it with indium nitride (InN) or aluminum nitride (AlN) produces emission with wavelengths ranging from green to deep ultraviolet. GaN-based multiple quantum well (QW) structures are used as the active regions of commercial light-emitting diodes and laser diodes. Such structures often exhibit bright-line emission despite very high dislocation densities. Recently, APT has been used to investigate the chemical and morphological microstructure of GaN- and GaAs-based structures (103–115).

It has been proposed that carrier localization can originate from structural and compositional effects such as quantum well width fluctuations and indium clustering (116). APT is ideally suited to describe compositional fluctuations and to look for nonrandom statistical fluctuations such as those proposed (18). A light-emitting diode (LED) device structure (50-nm p-GaN/30-mm GaN/3.5-nm In$_{0.15}$Ga$_{0.85}$ N QW/n-GaN) grown by metal-organic chemical vapor deposition on a semipolar (1011) GaN substrate was recently analyzed with APT (Figure 10) (110). Frequency distribution analyses were also performed (110) on the indium interatomic distances, and for this particular device structure, no evidence was obtained to cause rejection of the null hypothesis at the 95% confidence level. In other words, the indium composition fluctuations in this device were consistent with random fluctuations and could not cause carrier localization.
Figure 9
Specimens created from a commercially available 32-nm technology node CMOS device that was depackaged and then prepared by focused ion beam methods. (a) Atom probe tomography analysis shows a Hf-based high-k gate oxide near the top of the data set. (b) Regions of SiGe are visible on either side of a dominantly Si region. (b,c) Spatial distributions of the Ge, As, B, and C atoms. Whereas the As is distributed relatively uniformly (with a concentration of ~0.016 at%), the B is correlated with the regions of high-Ge content (96), and the carbon atoms appear to be clustered (72). (d) A high-angle annular-dark-field STEM image (97) (courtesy W. Lefebvre, Université de Rouen) of a structure similar to the one analyzed in panels a–c. An undercut of the gate oxide into the channel is apparent, matching the Ge distribution shown in panel b.

APT data have also been collected from a CdTe layer within a CdTe solar cell that was prepared with standard CdCl₂ and Cu treatments (117, 118). Figure 11 shows the mass spectrum, which contains a number of high-mass molecular ions. This spectrum is one of the most complex APT spectra published to date. Despite this complexity, crucial information concerning segregation of impurities at the grain boundaries has been found.

Ceramic and Geological Materials
Although various insulating or ceramic materials were first investigated with the pulsed-laser atom probe approximately 30 years ago (119), only recently has there been further research in this area.
The reemergence of pulsed lasers in APT analysis has opened the way for the analysis of bulk (or near-bulk) insulating oxides of various metals, including Al (120–122), Si (120, 123–125), Zr (126, 127), Ce (127–129), Li (127), Zn (130–132), In (133), Mg (132, 134), Fe (135), and Ni (E.A. Marquis & R. Reed, unpublished work). Some studies directed more toward the theory of field evaporation of such materials have also been published (136–138). Several examples of the application of APT to ceramic materials in materials science are presented in this section.

Carbon at low levels can be difficult to detect by electron microscopy and, as such, has traditionally been a very strong area of research for APT (18, 33). SiC additions improve the mechanical properties of alumina even at low particle volume fractions. APT was recently used to analyze grain boundaries in alumina to investigate the position of carbon atoms with respect to grain boundaries (122). A site-specific FIB preparation was used to position a grain boundary in the near-apex region of a specimen. APT analysis shows a level of carbon segregation of $1.5 \pm 0.5$ atom nm$^{-2}$ with no measurable carbon found within the alumina grains. The matrix alumina composition was measured to be $43.5 \pm 1$ at% Al–$56.5 \pm 1$ at% O with less than 2 at% H (Al/O ratio is $0.77 \pm 0.3$ as compared with the expected value of 0.67) (122). One possible explanation for the missing oxygen is that it may be present as $^{16}$O$_{2}^{++}$ counts at m/n = 16 Da, and thus the $^{16}$O$^{+}$ peak is counted as all single oxygen ions when some counts may in fact be double oxygen ions.

In addition to bulk alumina, APT has recently been used to investigate metal/oxide interfaces, namely the oxide films formed on a metal surface or along grain boundaries. Elements such as Hf, Ta, and Si contribute to improving the oxidation resistance of Ni-base superalloys. Whereas Hf may be imaged at Al$_2$O$_3$ grain boundaries by STEM-EDX (139), APT analysis also reveals a distribution of other dopants (Ta and Si) at the oxide/metal interface, at oxide grain boundaries, and within the oxide grains (Figure 12a). Figure 12b shows Zr, Hf, and Y segregation at a grain boundary in the thermally grown Al$_2$O$_3$ scale formed on a Ni-base superalloy (Y. Chen, E.A. Marquis & R.C. Reed, unpublished work).

Segregation at grain boundaries is also of interest in doped Ce-based oxide materials, which are being investigated as an electrolyte in solid-oxide fuel cells. To explain the decrease in...
Figure 11

(a) Atom probe tomography spectrum and (b) three-dimensional atom maps of CdS, CdCl, and TeS molecular ions, with a color overlay of CdCl (orange), Cd (black), Te (dark green). These two-dimensional renderings show enrichment of S and Cl at the grain boundary. Quantitative composition profiles that were generated from the dashed-box region show peak Cl concentrations at the grain boundary to be well over 1 at% and S concentrations of approximately 0.5 at%, which are very large amounts for impurities. Reprinted with permission from Reference 117. Copyright 2012, Cambridge University Press.
ion conductivity in fuel cells, Li et al. (129) recently used APT to investigate segregation to grain boundaries in sintered doped CeO$_2$. They found a depletion of Ce and an increase in Y (Figure 13) or Gd (140) at the grain boundaries in these materials.

Given the success of synthetic ceramic materials analysis with APT, geological materials are a natural next step. Analyses of metamorphic magnetite (141), natural olivine (142), calcium carbonate (143), and ancient zircons (D. Snoeyenbos & D. Reinhard, private communication) have been conducted, but this field is just getting established. One illustrative example of the value of APT to geology comes from an exogeology application: analysis of (Allende) meteoritic nanodiamond grains (144). In this work, the isotope ratios for carbon have bearing on theories of their cosmic origin, particularly whether they are solar or presolar. Isolated nanodiamond particles were embedded in Pt and then prepared by FIB lift-out for APT analysis. Figure 14 is an atom map that shows the resulting composite. Standard terrestrial carbon isotope ratios for $^{12}$C/$^{13}$C are 92.4. Stadermann et al. (144) found $^{12}$C/$^{13}$C = 61 ± 4 for C$^+$ and $^{12}$C/$^{13}$C = 54 ± 4 for C$^{++}$. Although this work is considered preliminary and these isotope ratios must be validated, it...
Figure 13

(a) Atom map of Y (green), Ce (red), and oxygen (blue); the analysis volume includes a triple junction (129). (b) A concentration profile across a portion of the grain boundary. Volume shown as “A” is also shown in panel b and exhibits clear segregation of Y, which Li et al. (129) determined to be 2–4 at% higher (depending on boundary region i, ii, or iii denoted in panel a) than the Y content within the grains. The total average concentration of Y, Ce, and O in these data was determined to be very close to the expected nominal composition. Reprinted from Reference 129 with permission from Elsevier.

does illustrate the potential impact that APT can have on such studies. Despite the challenges nanoparticles present for specimen preparation for APT, Stadermann et al. (144) have developed a working approach.

Organic and Biological Materials

A recent article (145) recounted the history of attempts to analyze organic materials with APT. A couple of examples are provided here to illustrate the state of this art. Synthetic polymers, such as self-assembled monolayer-forming oligomers (146–148), larger-molecular-weight polymers (149), and natural biopolymers (145) made from assemblies of proteins to make subcellular systems, have yielded to APT analysis. The potential to access nanoscale chemical imaging information on these complexly organized materials promises to open up a new understanding of interchain interactions and of interfacial interactions that are important in organic device development (150) and biology.

One issue of larger concern for APT analysis of polymeric materials is the potential for large molecular-ion evaporation. The spatial precision of the three-dimensional reconstruction is partially predicated on ion size. For atomic ions, maximum spatial precision is achieved, whereas for large molecular ions, all the atoms composing the molecule are essentially placed at the same position in three dimensions—no molecular orientation information can be collected (146). The complexity of polymer microstructures leads to field-evaporated mass spectra with a wide variety of ion sizes and thus to reduced spatial precision relative to monatomic ions. An example of this variety is evident in mass spectra from poly(3-hexylthiophene) (P3HT) films and prepared for APT by different methods (Figure 15a) (149). For thin films deposited on carrier tips, large molecular-ion fragments are observed, whereas for FIB-extracted sections, primarily monatomic and diatomic ion species are detected. Ion fragments are observed for nearly every integer mass position, but there are no peaks representing single-carbon ions. For P3HT films doped with
C$_{60}$ molecules, both fragmented and whole C$_{60}$ ions were observed, with the relative abundances varying as a function of analysis conditions (see Figure 15a).

Composite P3HT and [6,6]-phenyl-C$_{61}$ butyric acid methyl ester (PCBM) films, a popular bulk heterojunction material for organic photovoltaic devices such as solar cells (150), were deposited and prepared via FIB lift-out. Chemically, these are similar in composition and structure to the C$_{60}$-doped films described above; however, the mass spectra collected from these films are starkly different, as shown in Figure 15b. Here, carbon is a dominant monatomic ion, and atomic-mass ions with m/n > 60 are absent from the mass spectrum. This is consistent with mass spectra observed from other FIB-prepared polymer specimens, including cell biopsies where atomic carbon, nitrogen, and oxygen were observed with very few large-mass ion fragments (151).

The most advanced analysis of a biological material comes from the recent work of Gordon & Joester (152) on chiton teeth. Specimens were FIB extracted from the cutting edge of magnetite-based teeth, which contain 5–10-nm-diameter chitin protein fibers. The mass spectra were logical for the materials and showed clearly distinct peaks from the organic and mineral components. Atom maps of two analyses are shown in Figure 16. The organic-matter-derived ions are clearly seen to originate from fibers occluded within the mineral. The total amount of carbon is less than what would be expected from crystalline chitin fibers, which may be a consequence of overlapping peaks in time-of-flight spectra, preferential evaporation, or biological remodeling of fibers during mineralization. Nevertheless, the fiber diameter (5–10 nm) closely resembles that of the organic fibers observed in STEM images of the mineralized tooth. Furthermore, Na and Mg clearly colocalize with organic fibers (Figure 16b,c and Figure 16e,f, respectively).

All the examples of organic materials analysis by APT are from specimens prepared at room temperature. For a general organics capability, it will be important to prepare specimens at cryogenic temperatures and then to transfer them to the atom probe while keeping them cold and clean. Cryo-preparation stages for FIBs and cryo-transfer vacuum vessels from FIBs to a CAMECA LEAP$^\text{TM}$ are now commercially available (for example, see

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**Figure 14**
Atom map of several clusters of meteoritic nanodiamonds (arrow) embedded in Pt. Shown is a 2-nm-thick slice cut through the data set along the plane of the original diamond deposition layer.
Figure 15

(a) Typical mass spectrum for C_{60}-doped poly(3-hexylthiophene) (P3HT) polymer, highlighting the rich distribution of ion fragments observed for polymer films deposited on sharp carrier tips. (Inset) Expanded mass-to-charge-state-ratio range showing the large number of C_{60} ions observed. (b) Mass spectrum for [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM)-doped P3HT sample prepared by focused ion beam lift-out extraction from a spin-coat-deposited film. The ion fragment distribution has fewer peaks and chemical species such as individual carbon ions that are unambiguously identifiable. The chemical structures for PCBM and P3HT are also shown (inset). Reprinted with permission from Reference 160. Copyright 2012, Cambridge University Press.

http://www.leica-microsystems.com/products/electron-microscope-sample-preparation/industrial-materials/transfer/details/product/leica-em-vct100/). The EMEZ (Electron Microscopy ETH Zurich) facility at ETH Zurich and the Electron Microbeam Analysis Laboratory at the University of Michigan are the first laboratories to be equipped for this type of work and are operational as of early 2012. Although cryogenic micromanipulation is not yet commercially available, commercial suppliers are aware of the need. It is the final hardware item needed for full cryogenic specimen preparation of specimens. Once available, these hardware advances will enable full cryo-preparation, which may be the final step in the pursuit of APT analysis of organic specimens.
**CONCLUDING REMARKS**

APT has matured over the past decade to become an essential microanalytical technique for research on a wide spectrum of materials. It is presently being adopted for, and adapted to, manufacturing needs in the microelectronics industries, which would be the next step in maturation of the technology. As a class of materials, organic and biological materials are the next frontier for application of APT technology. If subnanometer compositional mapping of biological materials in 3D becomes a reality, the impact of such new information on the creation of knowledge could be profound.

With all the improvements in APT technology over the past decade, what are the remaining development needs? Prior to 2000, data-collection times were the bottleneck, as several days could be needed to collect an image. Now with improved speed, data collection takes hours, and the bottleneck has shifted to specimen preparation on the front end and data reconstruction and analysis on the back end. Automated methods need to be developed both to speed the process and to increase the uniformity of the results. Development work on these topics will likely lead to much progress in the next few years. For example, automation of specimen preparation in an FIB is expected, as is use of multivariate statistical analysis methods (153, 154) for data analysis. In the Future Issues section below, we discuss the two most serious limitations of APT today: specimen yield and data-reconstruction fidelity.
Given today’s state of the art, it is now possible to envision a time when 100% of the atoms in a large volume (≫10^6 nm³) of material will be positioned in three dimensions with high precision (3) that takes APT into the realm of atomic-scale tomography. Although APT offers high-value microanalytical information today, it still has tremendous upside potential. The next decade should be a continuation of exciting times for the field.

**FUTURE ISSUES**

**Specimen-Yield Challenges**

Sometimes, when one is working with an unfamiliar material or structure, specimen yield is low initially and increases with trial and experience. The challenge is to climb this learning curve quickly by avoiding or overcoming difficulties. In the present context, specimen yield refers to the probability of obtaining useful amounts of quality data from a specimen before failure. Because the stress in an atom probe specimen varies with the square of the applied electric field and is generally close to the cohesive strength of materials, any weakness in a specimen can lead to fracture failure. For specimens with specific regions of interest, any specimen will yield approximately in proportion to the ratio of the strength/adhesion in these regions of interest to the field-induced stress at the operating field. Fundamentally, the only way to improve yield is (a) to reduce the stress on the specimen or (b) to increase strength/adhesion.

There are some general ways to decrease evaporation field, and hence stress, in a specimen:

1. decrease ion detection rate (lower evaporation field),
2. increase the background (or other) gas pressure in the vacuum chamber,
3. increase specimen base temperature,
4. use laser mode rather than voltage pulsing, and
5. increase laser energy.

General methods to increase strength/adhesion include the following:

1. change the orientation of the features of interest (e.g., interfaces) in the specimen, such as a change from plan view to cross-section view,
2. remove materials that are not of general interest and that have highly different evaporation characteristics,
3. coat (or etch then coat) the specimen with a layer of material, and
4. heat the specimen slightly following preparation.

Discontinuities in a specimen, such as an interphase interface, grain boundaries, a notch, or any high-stress distribution, can be initiation points for failure. Avoidance of such weaknesses, where possible, is often a successful strategy. For example, layered structures with phases known to have a high evaporation field or a weak interface with other phases can sometimes be eliminated from a structure. Furthermore, the orientation of the structure may be altered to run either bottom-side up so that the offending phase is encountered at the end of a run or in a cross-sectional orientation so that any weak interface is subject to lower stresses. The cross-section geometry, however, is subject to greater lateral trajectory aberrations that may diminish the spatial resolution across an interface.

Two further directions for ameliorating these problems that are currently receiving attention are to coat specimens after FIB preparation and to develop more sophisticated instrument control protocols that use real-time detector information to anticipate approaching problems and adapt accordingly.
Reconstruction Challenges

The ability to accurately reconstruct original spatial positions of field-evaporated ions emitted from a surface is fundamental to the success of APT. Understanding the evolution of tip shape and projection during field evaporation plays an important role in improving reconstruction.

Different phases, or even similar phases with different crystal directions, will field evaporate differently, leading to topological features on the specimen apex. Because the specimen is the primary optic in this projection microscope, these features lead to nonuniform magnification in the image. Several groups are working to improve existing reconstruction algorithms to account for these complexities. In extreme cases, ions from the different phases may cross paths, and information about their true relative location on the specimen may be corrupted.

State-of-the-art reconstruction algorithms use a simple point-projection method to position detected ion events back onto a hemispherical surface. The \( z \) increment for each reconstructed ion position \((x, y, z)\) is a simple function with respect to the detector impact position \((x, y)\) and ion sequence \((z)\) (4, 155–157). This method works well for limited field-of-view reconstructions of homogeneous materials. However, as the field of view is increased, the surface curvature deviates further from that of a hemisphere, and the single point projection poorly approximates a constant angular magnification. In addition, the nonhemispherical nature of the specimen apex shape is further complicated when materials of differing evaporation fields are simultaneously exposed on a tip surface. The combination of these effects makes it difficult to achieve an accurate reconstruction of atomic planes, even for a homogeneous, single evaporation-field material, over the full field of view (4, 5). For nanostructured materials with variations in evaporation field throughout the volume (e.g., multilayer films, precipitates, microelectronic-device structures), the problem is more significant (158). Flat interfaces or spherical precipitates can become highly aberrated and misshapen in the reconstruction. A reconstruction method mitigating these aberrations may require discarding simple projection-onto-hemispherical-surface methods in favor of methods that properly transform detector hit positions onto accurate representations of the evolving specimen surface.

In principle, reconstruction of APT data can be perfected with sufficient knowledge of the specimen evaporating-surface shape (specimen apex shape) during an experiment if ion crossing (159) is not present in the data set. To improve reconstruction accuracy, next-generation reconstruction methods need to make use of increasingly realistic specimen apex shapes and improve the understanding of how these surfaces project onto the detector and evolve during further evaporation of the tip surface. A program has been proposed (1–3) to develop an experimental capability to obtain images of the specimen apex region with sufficient detail to improve reconstruction. Simulations of the evolving specimen during field evaporation could also provide the apex shapes needed if a suitable model of the specimen can be found. The specimen model might be an educated first guess without experimental input, a result derived from the first reconstructed result of the data, or a model derived from experimental imaging of the specimen. Iteration between reconstruction and model refinement might then yield convergence. In either case, some form of specimen apex shape rendering is likely to play a role in reconstruction in APT going forward.

SUMMARY POINTS

1. Major progress has been made on hardware configurations for APT so that present-day commercial atom probes have become practical instruments. There have been major increases in data-collection rates of four orders of magnitude (to \( 5 \times 10^6 \) atoms min\(^{-1}\)), in field of view of two orders of magnitude (to \( 3 \times 10^4 \) nm\(^2\)), and in mass-resolving power of an order of magnitude (to >1,500) since 2000.
2. Laser pulsing has broadened the application of APT from metals and alloys to semiconductors, ceramic and geological materials, and organic and biological materials.

3. Specimen preparation for APT has become straightforward (with a FIB) such that site-specific analyses may be obtained routinely from such material features as grain boundaries and processed transistors in integrated circuits.

4. APT is often used in correlative microscopy efforts in which a strong synergy with SEM, TEM, SIMS, and EPMA has been demonstrated. On matters for which other analytical techniques can provide similar information, very good agreement has been found.

5. APT offers unique information in three dimensions at the atomic scale; such information often provides valuable insights into materials. In so doing, APT is transforming microscopy at the atomic scale.

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