Progress in the Atomic-Scale Analysis of Materials with the Three-Dimensional Atom Probe

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Introduction

Exactly 50 years ago, E.W. Müller became the first person to observe single atoms, with the aid of the field-ion microscope (FIM).[1] In 1967, with John Panitz and S. Brooks McLane, Müller's invention of the atom probe meant that, in his words, "We can now really deal much more intimately with the individual atoms which we encounter, since we know their names."[2] By combining position-sensitive detection with the time-of-flight mass spectrometry of single atoms in the atom probe, Cerezo and co-workers in the late 1980s built an instrument capable of reconstructing the three-dimensional (3D) atomic distribution of elements present in a material.[3] The instruments that are capable of microanalysis at this level, called generically 3D atom probes (3DAPs), were the subject of two articles published in *MRS Bulletin* in 1994.[4,5] In this article, we review some of the progress in the field since that time, in particular, the expansion of the range of materials problems that can be addressed by this powerful technique.

Instrument Design

The basic principle of the 3DAP is very simple. As in the FIM, specimens for the 3DAP are in the form of sharp needles of 50–100-nm end radius. The specimen is held at cryogenic temperatures (<100 K) in an ultrahigh-vacuum chamber at 0.5–1.0 m from a position-sensitive detector capable of detecting the impact of single ions (Figure 1). It is primarily the design of the position-sensitive detector that distinguishes the various 3DAP instruments.[3,6,7] A combination of high dc voltage and nanosecond-long high-voltage pulses raises the electric field at the apex of the specimen to a level where individual atoms are ionized and removed. The ions are emitted from the specimen along nearly radial paths, so the instrument acts as a simple point-projection microscope with very high magnification (several million times). Thus, the position of impact of an ion on the detector relates directly to its original surface position, and time-of-flight mass spectrometry is used to identify the ion. As atoms are removed, an elemental map of the top atomic layer is built up, with subnanometer spatial resolution. Continued removal produces atomic-layer-by-atomic-layer sectioning of the specimen and generates a full 3D reconstruction of the element distributions within the material.

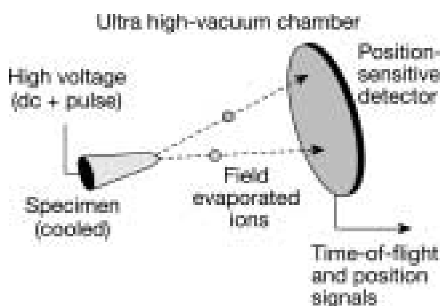

Figure 1. Schematic illustration of the design of a three-dimensional atom probe (3DAP).

Analysis of Nanophase Alloys

An example of the ultrafine-scale information available with the 3DAP technique is shown in Figure 2, which is a section from an analysis of an Al-1.9wt%Cu-0.3wt%Mg-0.2wt%Ag alloy aged at 180°C for 10 h, as reported by Reich et al.[8] An Ω-phase plate has formed in the alloy, with a thickness of approximately 10–13 $\{111\}_\alpha$ layers, corresponding to 3 unit cells of Ω. Not only can segregation of Ag and Mg to the α/Ω interface be clearly observed, but an interface step is also apparent. The concentration of Cu in the matrix immediately ahead of the step is higher than in the matrix far from the precipitate, and this indicates a process of redissolution as the precipitate shrinks during the coarsening process. This result illustrates the detailed, ultrahigh-resolution chemical information that is available with the 3DAP.

Early 3DAP instruments suffered from relatively poor mass resolution due to the energy variations resulting when ions are accelerated during a voltage pulse. In conventional atom probes, this problem had been solved by the incorporation of an energy-compensation scheme,[9] but the larger acceptance angle in a 3DAP initially made this difficult. Cerezo and co-workers solved the problem by building an instrument with a large-acceptance-angle reflectron lens (a type of ion mirror); this remains the state of the art in 3DAP design.[10] The improvement in mass resolution, combined with a high signal-to-noise ratio, allows quantitative analysis of advanced engineering alloys, where elemental peaks are often closely spaced in the mass spectrum. In the section of a mass spectrum from the stainless maraging steel 1RK91 (Fe-13at.%Cr-8.7at.%Ni-0.73at.%Al-1.1at.%Ti-1.8at.%Cu-2.3at.%Mo) shown in Figure 3, the peaks of Ni, Cu, and Mo are clearly separated, despite these elements being present at the percent level and separated by only one-sixth of a mass unit in some cases.[11]

An elemental map from an analysis of 1RK91 aged for 100 h at 475°C (Figure 4), shows that both Cu and Ni+Al+Ti precipitates are formed, the latter having a composition equivalent to $Ni_3(Al, Ti)$. The composite precipitate takes on a spherical shape, with a flat internal interface between Cu and $Ni_3(Al, Ti)$, clearly indicating

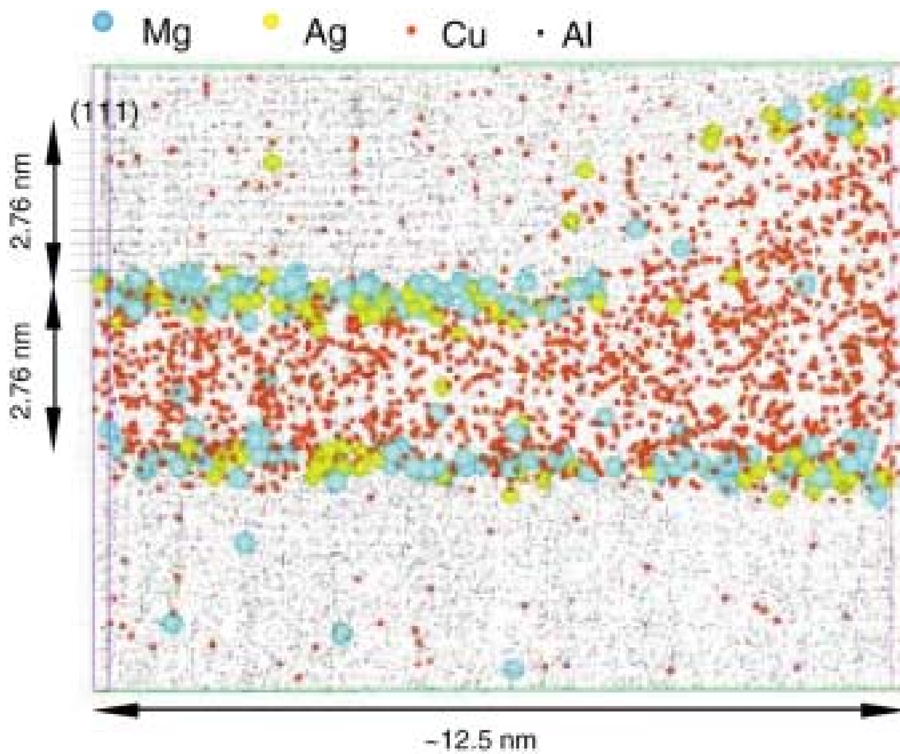

Figure 2. 3DAP elemental map showing a step at the interface of an Ω-phase precipitate formed in an Al-1.9wt%Cu-0.3wt%Mg-0.2wt%Ag alloy aged at 180°C for 10 h.[36] Segregation of Mg and Ag to the precipitate interface is clearly observed, as is the enhancement of Cu in the vicinity of the step. (Courtesy H. Hono, National Research Institute for Metals, and Acta Materialia.*)*

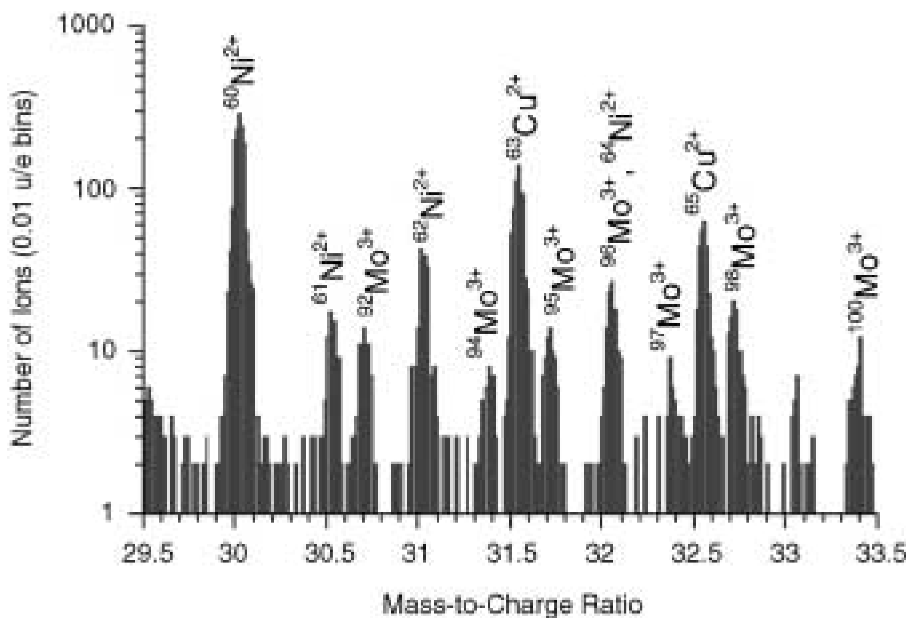

Figure 3. Section of a mass spectrum from the 3DAP analysis of the stainless maraging steel 1RK91 (Fe-13at.%Cr-8.7at.%Ni-0.73at.%Al-1.1at.%Ti-1.8at.%Cu-2.3at.%Mo). The large peaks due to Fe, Cr, and the main Ni isotope are not shown. (Courtesy Rev. Sci. Instrum.*[10]).*

that the Cu/Ni_3(Al,Ti) interface energy is much lower than that between either phase and the matrix. Results from earlier stages in the heat treatment show that the Cu precipitates are the first to form,[12] with the Ni_3(Al,Ti) precipitates nucleating heterogeneously on the Cu. At that stage, atomic planes are seen to be continuous between the precipitates and the matrix, so that the Cu precipitate appears to act as a template for the nucleation of the Ni_3(Al,Ti) phase.[13] The 3DAP clearly provides a unique combination of chemical, morphological, and crystallographic information, which can lead to unique insights into the details of solid-state phase transformations in alloys.

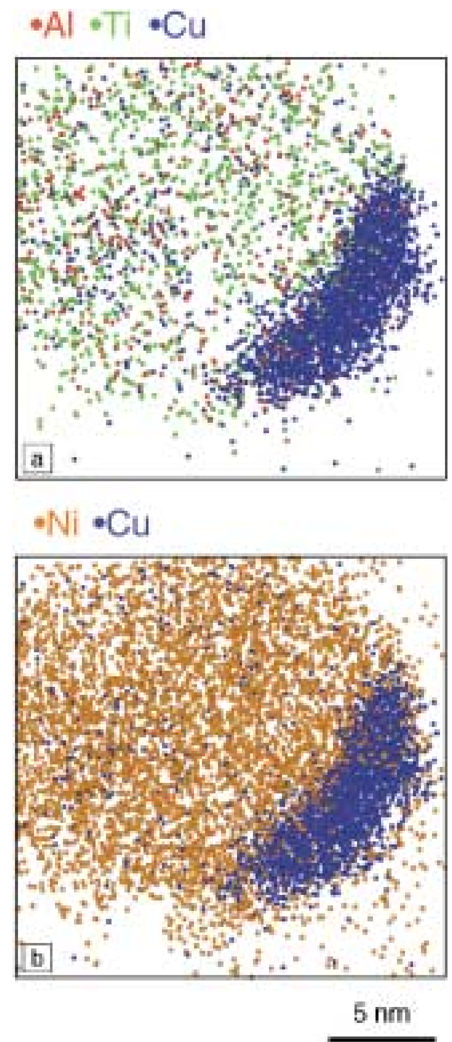

Figure 4. Elemental maps of (a) Cu, Al, and Ti, and (b) Cu and Ni from the analysis of the stainless maraging steel 1RK91 (Fe-13at.%Cr-8.7at.%Ni-0.73at.%Al-1.1at.%Ti-1.8at.%Cu-2.3at.%Mo) aged for 100 h at 475°C.

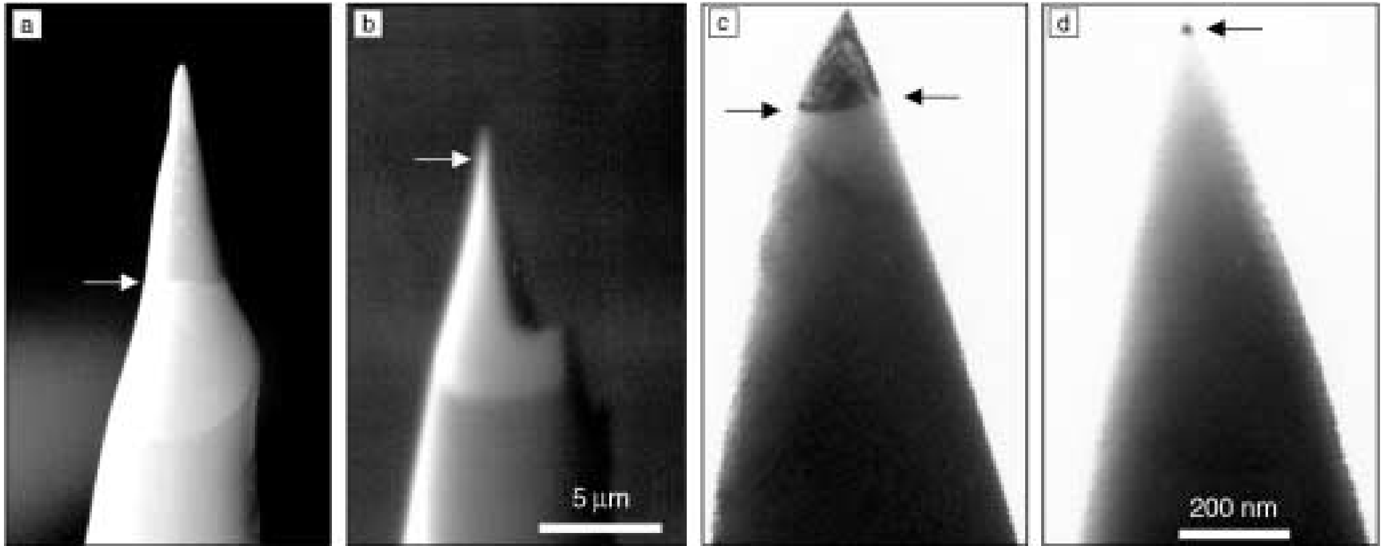

Figure 5. (a), (b) Secondary-ion images of a specimen of an "interstitial-free" (IF) steel (a) before and (b) after focused ion-beam (FIB) milling, showing how a sharp point is formed at the position of the grain boundary (arrows) by means of a series of cuts (at right of image). (c), (d) Transmission electron micrograph of the same specimen, (c) immediately after FIB milling and (d) after conventional ion milling, to complete the specimen preparation. Arrows point to the same spot on the sample.

Grain-Boundary Segregation

3DAP analysis of sparse microstructural features is made difficult by the small specimen volume, which limits the probability that a feature will be present in the apex region of a specimen made at random. For studies of grain boundaries in large-grained material, it is usually necessary to pre-select specimens through examination in a transmission electron microscope (TEM). This is often combined with removal of small amounts of material either by pulsed electropolishing or ion-beam milling, until the boundary is within the region of analysis.[14] Recently, focused ion-beam (FIB) milling has been used to simplify this laborious process.[15] The preparation of a specimen with a grain boundary using FIB milling is shown in Figure 5. Unfortunately, the resolution of the FIB does not usually permit observation of the exact position of the grain boundary once it is within a few hundred nanometers of the apex of the specimen, so the final stages are best completed using conventional ion-beam milling and TEM observation.[16] This combination also has the advantage of removing gallium implantation and "knock-on" damage resulting from the high-energy gallium ion beam used in FIB milling. It is hoped that future development in FIB technology will allow the whole process to be carried out in one instrument.

A 3DAP analysis from a grain boundary in an "interstitial-free" (IF) steel containing 7 ppm boron by weight is shown in Figure 6.[15] IF steels are of great interest for

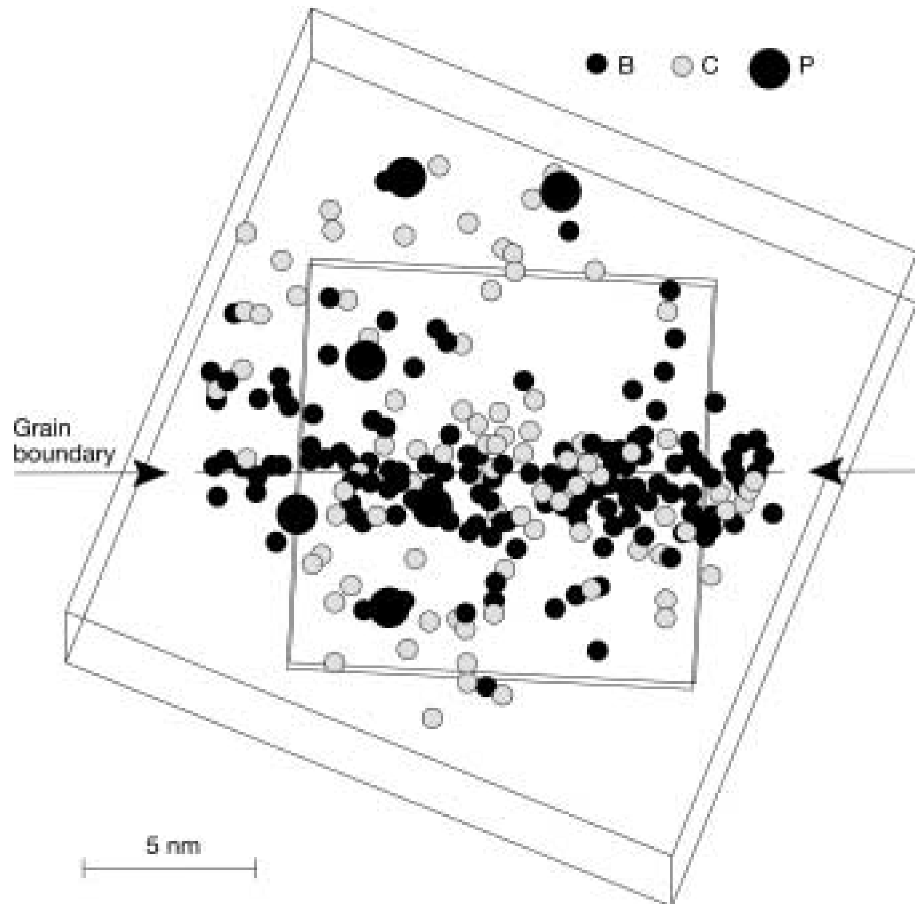

Figure 6. 3DAP analysis of a grain boundary in a field-ion specimen of an IF steel containing 7 ppm boron by weight, showing strong segregation of boron and carbon to the boundary and weak segregation of phosphorus.

deep-drawable sheet applications in the automotive industry; however, the lack of carbon at grain boundaries can generate problems of cracking during high-strain-rate forming operations. Small additions of boron have been found to alleviate some of these problems. From the data in Figure 6, there are 82 excess boron atoms and 63 excess carbon atoms over an analyzed area of approximately 112 nm^2, which gives Gibbsian interfacial excess measurements of 7.5×10^{17} atoms/m^2 for boron and 5.7×10^{17} atoms/m^2 for carbon. Note that the segregation is not confined to a single atomic layer, but is spread over 1 nm or so. The segregation of boron to the boundary appears to compensate for the lack of carbon, improving grain-boundary cohesion. The atom probe is unique in its capability for light-element analysis at non-embrittled boundaries.

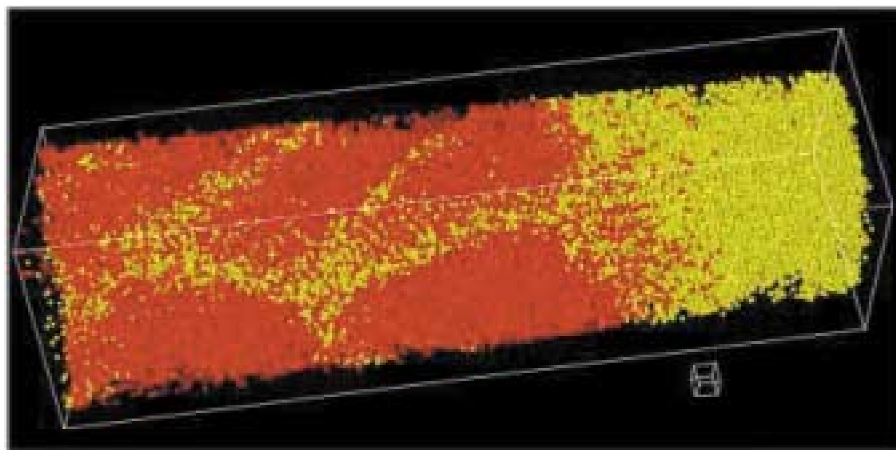

Figure 7. 3DAP elemental maps of Al (yellow) and Ag (red) from the analysis of an Al/Ag bilayer sputtered on a W field-ion specimen and annealed at 100°C for 15 min. Diffusion of Al along the grain boundaries in the Ag layer is evident. The scale of the image is given by the small 1 nm × 1 nm × 1 nm cube on the bottom right of the image. (Courtesy J. Schleiwies and G. Schmitz, University of Göttingen.)

Studies of Thin Films

The requirement of needle-shaped samples for 3DAP analysis is a particular problem in the study of thin-film materials, where the total thickness of the region of interest may be only a few nanometers. Historically, the solution has been to deposit thin-film layers directly onto the ends of preformed specimens. In the study of functional materials, this is less than ideal because the structures formed are likely to be different from those grown on planar substrates. However, this technique can produce unique insights into the process of interdiffusion and solid-state reactions at interfaces between deposited films, as has been elegantly shown by Schleiwies and Schmitz. An example of their work is illustrated in Figure 7, which shows a bilayer of Ag and Al deposited onto a W specimen and annealed at 100°C for 15 min. The Al has clearly diffused along the grain boundaries in the Ag layer, but the converse has not occurred. Detailed chemical analysis shows the composition near the grain boundaries to be Al_2Ag, although the equilibrium phase is $AlAg_2$.[17]

For successful application of 3DAP to the study of functional layers and devices, specimen-preparation techniques need to be used that allow needle-shaped samples to be fabricated from materials grown directly on planar substrates. Hasegawa et al. used photolithographic methods to form a specimen blank in a 2-μm Co-Cr layer.[18] They subsequently used electropolishing to sharpen the end of the blank, and obtained the first 3DAP analysis from such a material. A similar method was used by Larson and co-workers to study a Cu-Co multilayer stack with layer thicknesses of 2 nm and a total thickness of 400 nm.[19] In this work, the final polishing was performed by FIB milling.[20] This method has the disadvantage of producing implantation and knock-on damage in the layers, but this could be characterized directly from the 3DAP analysis. The layers were found to have significant conformal roughness, and the 3DAP images showed evidence of Co shorting across the Cu layers. These microstructural observations helped explain the high coercivity measured for the layers, which suggested significant ferromagnetic coupling between Co layers, although the Cu layer spacing of 2 nm was originally chosen to give antiferromagnetic coupling.

More recently, Larson and colleagues have developed an improved specimen-preparation method for the analysis of thin films.[21] The process uses a Si substrate on which a large number of columns have been etched. Layers deposited onto the substrate are capped with a protective metal film, and individual columns are broken off for mounting on the end of a pin. FIB milling[20] can then be used to sharpen the end of the resulting post, as shown in Figure 8, to make a specimen of the required sharpness. The metal capping layer protects the layers of interest from damage during this milling stage. The 3DAP analysis of a NiFe/CoFe/Cu/CoFe multilayer specimen prepared by this method is shown in Figure 9, including part of the capping layer and the first two repetitions of the multilayer.[22] A higher magnification view of a section of the analysis, Figure 9b, shows the individual (111) atomic planes within the film, together with the changes in chemistry across the four interfaces included in the section. Some features of the interfaces are clear just from this elemental map; for example, the CoFe/Cu interfaces are sharper than those between the NiFe and CoFe layers. However, the interface with CoFe growing on NiFe shows a more diffuse interface than that where NiFe is deposited on CoFe. More detailed analysis confirms that an asymmetry also exists for the CoFe/Cu interfaces, and the composition profile for Fe indicates that it is segregated to the surface of the growing CoFe layer.

The results shown here indicate the potential for the 3DAP analysis of thin-film materials. A number of studies have indicated the importance of interface roughness and intermixing to properties such as giant magnetoresistance (GMR),[23] but it has never been possible before now to study these two effects separately at sufficiently high resolution. Preparing 3DAP specimens by the method described here should permit analysis of films with a total thickness down to 50 nm or less, with no need for a special lift-off layer, and the results can be directly compared with property measurements from films deposited on other parts of the same wafer. The specimen geometry also gives maximum spatial resolution in the direction normal to the interface, which is usually desirable for accurate chemical and morphological characterization of the interfaces. With the ability to make specimens in this way, the 3DAP can make significant contributions to the understanding and optimization of properties in magnetic multilayer films.

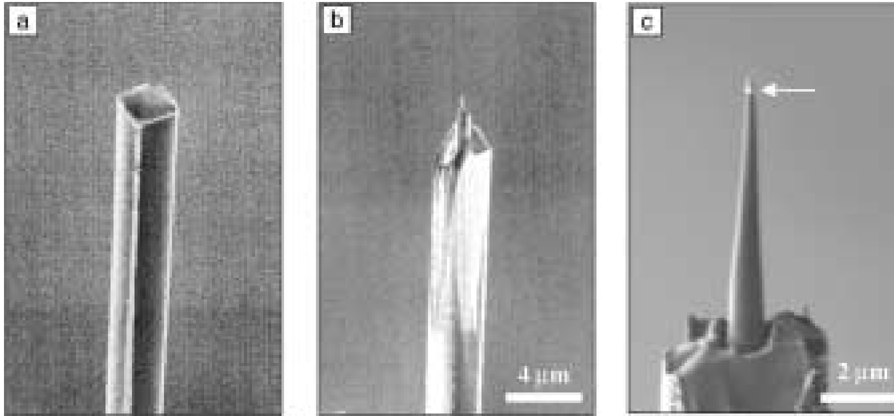

Figure 8. (a)–(c) Sequence of secondary-ion images during the preparation of a 3DAP specimen from a multilayer thin film. (a) Oblique view of the silicon post with layers deposited onto the flat end. (b) Similar view of the specimen sharpened by a two-stage annular milling. (c) Side view, showing the specimen more clearly. Note the bright contrast from the metallic layers at the specimen apex (arrow).

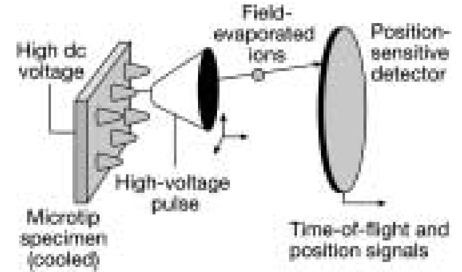

Figure 10. Schematic illustration of the scanning atom probe.

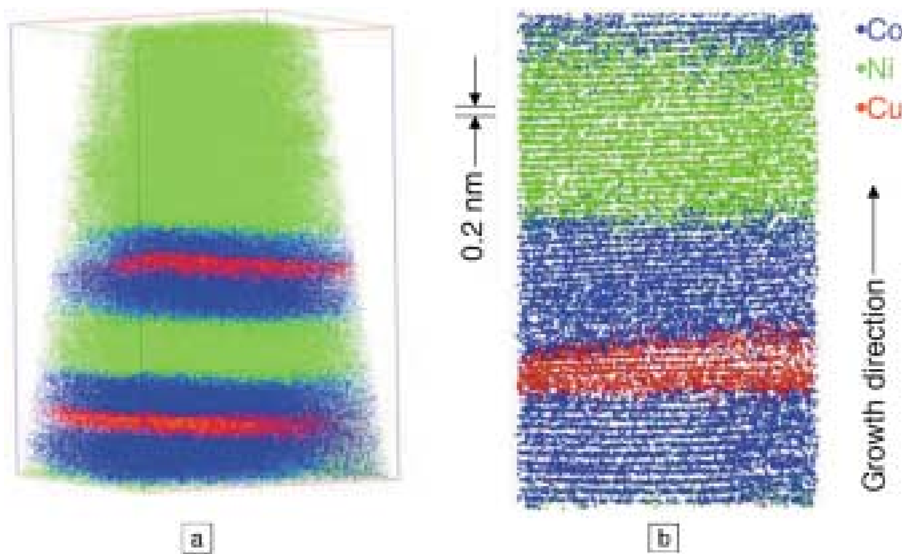

Figure 9. (a) Reconstruction of the 3DAP analysis of a NiFe/CoFe/Cu/CoFe multilayer thin-film structure. The Ni, Co, and Cu atom positions are shown by green, blue, and red dots, respectively. Height of the volume shown is approximately 35 nm. (b) Magnified view from a section of the analysis showing individual (111) planes along the growth direction.

What Next?

Work on thin-film materials and devices will be further enhanced by current instrument developments to allow use of specimens in the form of microtips fabricated on the surface of a planar substrate. The basic principle of this new instrument, known either as the scanning atom probe,[24] or the local electrode atom probe,[25] is shown in Figure 10. Microtip specimens are fabricated from thin films or devices on a planar substrate, either by masking and ion-beam milling[26,27] or by the use of FIB milling. Many hundreds of microtips could be made within a few mm^2, all with the layers of interest at the apex. However, to generate the necessary electric field for 3DAP analysis, a microelectrode needs to be brought close to one of the microtips. Without this, the presence of the flat substrate would limit the field at the apex and prevent the removal of atoms. Moving the microelectrode across the surface allows individual microtips to be addressed and analyzed in turn, maximizing the number of specimens that can be made from a given amount of material.

Results from the 3DAP still fall short of full atomic resolution, due to the presence of small trajectory aberrations (the source of which remains poorly understood) that reduce the lateral resolution.[28] It was thought that details of the way atoms move as they leave the surface and become ionized were at the root of the problem and that it would require quantum mechanical calculations to model these trajectories. However, work by Vurpillot and colleagues has shown that many of the features exhibited as a result of trajectory aberrations can be reproduced in a simple electrostatic model.[29,30] Warren and co-workers have also shown that, in certain cases, more crystallographic detail is present in the 3DAP analysis than was previously expected.[31] It may be that the understanding obtained from the electrostatic modeling can be used to correct for the aberrations and thus permit 3D reconstruction of elemental distributions with full atomic resolution. The measurements of segregation and heterogeneous nucleation shown here could then be coupled with detailed atomic measurements of interface structure.

In the materials science area, the development of computer modeling has enabled larger volumes of material to be simulated, using atomic-scale methods. This has been happening at the same time that the development in atom-probe methods has allowed the continuing increase of both the volume of material that can be mapped at the atomic scale and the quality of the data obtained. There is a convergence between these two very different approaches to the study of materials, and a number of combined experimental and modeling programs have been very successful.[32–35] In the 21st century, the combination of the three-dimensional atom probe with atomistic modeling may provide a springboard for the systematic de-

velopment of the next generation of alloys and metallic multilayer devices. Atomic engineering of these materials is now a realistic prospect.

Acknowledgments

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References

1. E.W. Muller, *Z. Phys.* **131** (1951) p. 136.
2. E.W. Muller, J.A. Panitz, and S.B. McLane, *Rev. Sci. Instrum.* **39** (1968) p. 83.
3. A. Cerezo, T.J. Godfrey, and G.D.W. Smith, *Rev. Sci. Instrum.* **59** (1988) p. 862; G.D.W. Smith and A. Cerezo, European Patent No. 0231247 (October 10, 1990).
4. D. Blavette and A. Menand, *MRS Bull.* **XVIX** (7) (1994) p. 21.
5. M.K. Miller and G.D.W. Smith, *MRS Bull.* **XVIX** (7) (1994) p. 27.
6. D. Blavette, B. Deconihout, A. Bostel, J.M. Sarrau, M. Bouet, and A. Menand, *Rev. Sci. Instrum.* **64** (1993) p. 2911.
7. A. Cerezo, T.J. Godfrey, J.M. Hyde, S.J. Sijbrandij, and G.D.W. Smith, *Appl. Surf. Sci.* **76/77** (1994) p. 374.
8. L. Reich, M. Maruyama, and K. Hono, *Acta. Mater.* **46** (1998) p. 6053.
9. E.W. Muller and S.V. Krishnaswamy, *Rev. Sci. Instrum.* **45** (1974) p. 1053.
10. A. Cerezo, T.J. Godfrey, S.J. Sijbrandij, P.J. Warren, and G.D.W. Smith, *Rev. Sci. Instrum.* **69** (1998) p. 49.
11. A. Cerezo, D. Gibuoin, S. Kim, S.J. Sijbrandij, F.M. Venker, P.J. Warren, J. Wilde, and G.D.W. Smith, *J. de Phys.* **6** (1996) p. C5-205.
12. K. Stiller, M. Hattestrand, and F. Danoix, *Acta Mater.* **46** (1998) p. 6063.
13. A. Cerezo, D. Gibuoin, T.J. Godfrey, J.M. Hyde, S. Kim, R.P. Setna, S.J. Sijbrandij, F.M. Venker, J. Wilde, and G.D.W. Smith, in *Proc. Int. Conf. "ICMFM 96,"* edited by N. Igata, Y. Hiki, I. Yoshida, and S. Sato (University of Tokyo Press, Tokyo, Japan, 1996) p. 281.
14. M. Thuvander and H.-O. Andren, *Mater. Charact.* **44** (2000) p. 87.
15. K. Seto, D.J. Larson, P.J. Warren, and G.D.W. Smith, *Scr. Mater.* **40** (1999) p. 1029.
16. D.J. Larson, K.F. Russell, and A. Cerezo, *J. Vac. Sci. Technol., B* **18** (2000) p. 328.
17. J. Schleiwies and G. Schmitz, to be published in *Mater Sci. Eng., A* (2001).
18. N. Hasegawa, K. Hono, R. Okano, H. Fujimori, and T. Sakurai, *Appl. Surf. Sci.* **67** (1993) p. 407.
19. D.J. Larson, A.K. Petford-Long, A. Cerezo, and G.D.W. Smith, *Acta Mater.* **48** (2000) p. 4019.
20. D.J. Larson, D.T. Foord, A.K. Petford-Long, H. Liew, M.G. Blamire, A. Cerezo, and G.D.W. Smith, *Ultramicroscopy* **79** (1999) p. 287.
21. D.J. Larson, R.L. Martens, T.F. Kelly, M.K. Miller, and N. Tabat, *J. Appl. Phys.* **87** (2000) p. 5989.
22. D.J. Larson, A. Cerezo, R.L. Martens, P.H. Clifton, T.F. Kelly, A.K. Petford-Long, and N. Tabat, *Appl. Phys. Lett.* **77** (2000) p. 726.
23. X. Portier and A.K. Petford-Long. *J. Phys. D: Appl. Phys.* **32** (1999) p. R89 and references therein.
24. O. Nishikawa and M. Kimoto, *Appl. Surf. Sci.* **76/77** (1994) p. 424.
25. T.F. Kelly, P.P. Camus, D.J. Larson, L.M. Holman, and S.S. Bajikar, *Ultramicroscopy* **62** (1995) p. 29.
26. J.A. Liddle, A. Norman, A. Cerezo, and C.R.M. Grovenor, *J. Phys. Colloq.* **49** (C6) (1988) p. 509.
27. D.J. Larson, C.-M. Teng, P.P. Camus, and T.F. Kelly, *Appl. Surf. Sci.* **87/88** (1995) p. 446.
28. M.K. Miller, A. Cerezo, M.G. Hetherington, and G.D.W. Smith, *Atom Probe Field-Ion Microscopy* (Oxford University Press, Oxford, 1996) p. 192–199; M.K. Miller, *Atom Probe Tomography: Analysis at the Atomic Level* (Kluwer Academic, New York, 2000) p. 148–152.
29. F. Vurpillot, A. Bostel, E. Cadel, and D. Blavette, *Ultramicroscopy* **84** (2000) p. 213.
30. F. Vurpillot, A. Bostel, and D. Blavette, *Appl. Phys. Lett.* **76** (2000) p. 3127.
31. P.J. Warren, A. Cerezo, and G.D.W. Smith, *Mater Sci. Eng., A* **250** (1998) p. 88.
32. M.K. Miller, J.M. Hyde, M.G. Hetherington, A. Cerezo, G.D.W. Smith, and C.M. Elliott, *Acta Metall. Mater.* **43** (1995) p. 3385; J.M. Hyde, M.K. Miller, M.G. Hetherington, A. Cerezo, G.D.W. Smith, and C.M. Elliott, *Acta Metall. Mater.* **43** (1995) pp. 3403 and 3415.
33. R.P. Setna, A. Cerezo, J.M. Hyde, and G.D.W. Smith, *Appl. Surf. Sci.* **76/77** (1994) p. 203.
34. C. Pareige, F. Soisson, G. Martin, and D. Blavette, *Acta Mater.* **47** (1999) p. 1889.
35. J.-M. Roussel and P. Bellon, *Phys. Rev. B.*, submitted for publication, 1999.
36. K. Hono, *Acta Mater.* **47** (1999) p. 3127.

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