Orientation and phase mapping in the transmission electron microscope using precession-assisted diffraction spot recognition: state-of-the-art results

D. VILADOT*, M. VÉRON†, M. GEMMI‡, F. PEIRÓŠ, J. PORTILLO∥, S. ESTRADÉ§, J. MENDOZA#, N. LLORCA-ISERN* & S. NICOLEPOULOS∥,*

*CPCM Universitat de Barcelona, Facultat de Química, Departament de Ciencia de Materials i Enginyeria Metallúrgica, Barcelona, Catalunya, Spain
†Laboratoire SIMaP, Grenoble INP – CNRS – UJF, Saint Martin d’Hères Cedex, France
‡Center for Nanotechnology Innovation@NEST, Istituto Italiano di Tecnologia, Pisa, Italy
§LENS, MIND-IN2UB, Departament d’Electrònica, Universitat de Barcelona, Barcelona, Spain
∥NanoMEGAS SPRL, Brussels, Belgium
#Centres Científics i Tecnològics de la Universitat de Barcelona, Barcelona, Catalunya, Spain

Key words. Precession-assisted crystal orientation mapping, precession electron diffraction, TEM orientation and phase mapping.

Summary
A recently developed technique based on the transmission electron microscope, which makes use of electron beam precession together with spot diffraction pattern recognition now offers the possibility to acquire reliable orientation/phase maps with a spatial resolution down to 2 nm on a field emission gun transmission electron microscope. The technique may be described as precession-assisted crystal orientation mapping in the transmission electron microscope, precession-assisted crystal orientation mapping technique—transmission electron microscope, also known by its product name, ASTAR, and consists in scanning the precessed electron beam in nanoprobe mode over the specimen area, thus producing a collection of precession electron diffraction spot patterns, to be thereafter indexed automatically through template matching. We present a review on several application examples relative to the characterization of microstructure/microtexture of nanocrystalline metals, ceramics, nanoparticles, minerals and organics. The strengths and limitations of the technique are also discussed using several application examples.

Introduction
The scope of this paper is the review of several nanometre-scale state-of-the-art applications obtained using the precession-assisted crystal orientation mapping technique (PACOM) – commercially, ASTAR – which is a Transmission Electron Microscope (TEM)-based diffraction spot recognition technique. Other existing techniques leading to orientation mapping in the TEM include: transmitted Kikuchi line pattern and recognition and conical dark field scanning imaging, both of which have specificities that hinder their wide applicability. Effectively, transmitted Kikuchi line pattern recognition is too sensitive to crystal defect density and to extreme thinness for nanometre-scale crystal mapping, whereas conical dark field scanning imaging requires large acquisition and processing times and suffers from dynamical contributions to the reconstructed spot patterns (Barmak, 2010; Zaefferer, 2011). Orientation and phase maps at micrometre level may nowadays be routinely obtained in the scanning electron microscope (SEM) with the electron backscatter diffraction (EBSD) attachment, which is an effective way to characterize a wide variety of bulk crystalline materials, with spatial resolution of typically 50 nm when using a field emission gun (FEG)-SEM. Moreover, recently a new technique, t-EBSD, has been developed (Keller & Geiss, 2011; Trimby, 2012) claiming resolution from 5 to 15 nm on FIB-prepared thin samples.

The goal for the continuous development of the PACOM (ASTAR) technique has been, ever since its first appearance in the materials research field (Rauch & Dupuy, 2005), to extend the wide applicability of the EBSD-SEM approach for orientation mapping into the nanometre-scale domain, specific to the TEM’s large magnification range. Effectively, when using the nanobeam diffraction mode and a small condenser aperture (10 or 20 µm), a high spatial resolution may be obtained on the specimen, down to a few nanometres in diameter, while
preserving enough beam brightness when using an FEG tip to reveal a neat spot pattern. The number of spots present in these patterns improves significantly when using precessed illumination as well as an intensity distribution closer to the kinematical diffracting condition. These two features usually allow solving the usual 180° ambiguity for orientation determination present in conventional nonprecessed transmitted spot patterns. Below, we present a review on several application examples using the ASTAR method at nanometre-scale level.

**Precession microscopy: pattern acquisition and identification**

For this rather new technique, sample preparation is the same as in standard TEM observations, although when seeking the best possible spatial resolution for orientation maps obtained on thin foils, a compromise between expected grain size and sample thickness along beam direction is advisable; the PACOM technique will not easily discriminate superimposed spot diffraction patterns originating from piled-up crystals along beam direction. During data acquisition, electron diffraction spot patterns are collected sequentially with a dedicated external CCD camera (attached to the TEM viewing screen) while the sample area (typically from a fraction to tens of square micrometres) is scanned by the incident quasi-parallel nanobeam (<2 mrad). The latter is simultaneously precessed around the optical axis of the microscope to reduce strong dynamical effects, as can be seen schematically in Figure 1(A). In precession electron diffraction (PED), the incident rotating beam describes a cone, the pivot point of which is focused on the sample; this produces a hollow-circle array of diffraction spots at the exit plane of the sample, but when a counterprecession signal is applied and adjusted at the level of the back focal plane of the objective lens, a pseudostatic diffraction image is retrieved. Simultaneous beam scanning (translation) and precession diffraction are generated by a dedicated external hardware unit, which also allows the control of the beam pivot point (Rauch, 2008).

The reason for using beam precession is that it has been shown that PED results in an increased number of reflections, which exhibit a quasi-kinematical integrated intensity (Vincent & Midgley, 1994). This method may also cause higher-order Laue zone reflections to become excited, depending on crystal tilt with respect to the beam as well as on lattice parameter. An example of these two improvements is shown in Figure 2, where the [001] diffraction pattern of a mayenite crystal, tilted 10° off the <001> direction; note increased number of exited spots in both, zero- and first-order Laue zone.

![Figure 1](image1.png)  
**Fig. 1.** Schematic illustration of the tool system: (A) the beam is precessed at a high rate and (B) scanned over the area of interest. The diffraction patterns (C) improved by precession (D) are compared to simulated diffraction patterns to recognize phase and orientation; (E) overview of the ASTAR hardware components and colour-coded inverse pole figure.

![Figure 2](image2.png)  
**Fig. 2.** Mayenite [001] (A) static electron diffraction pattern and (B) precessed electron diffraction pattern. Patterns correspond to a cubic mayenite crystal with lattice 11.95 Å, space group I-4 3-d, tilted 10° off the <001> direction; note increased number of exited spots in both, zero- and first-order Laue zone.
Fig. 3. Precession angle-dependent beam broadening: vertical axis shows focused beam diameter ($\Phi$) in nanometres and horizontal axis, precession angle ($\alpha$) in degrees. Inset figures (A), (B) and (C) display focused beam shape as viewed in the TEM fluorescent screen when imaging mode. Figure obtained on a 200 kV FEG-TEM fitted with a high-resolution pole piece, choosing quasi-parallel nanobeam illumination through a second condenser lens aperture of 10 $\mu$m.

the instrumental point of view on two parameters: the effective focused beam size on the thin specimen and the scanning step chosen for rastering the beam. The former parameter (shown in Fig. 1B as round white dots) is defined not only by the condenser system available in the TEM and the smallest condenser aperture available, but also – when using precession – by the beam broadening introduced by the microscope spherical aberration for the nonaxial trajectories. A typical beam broadening curve for an FEG type of 200 kV TEM fitted with a High-Resolution pole piece, with a 10 $\mu$m size second condenser lens aperture is shown in Figure 3. The combination of precession at 0.6° and uncorrected spherical aberration turns an original 2 nm focused spot into a 4-nm-wide one. If a rastering step of half this value is chosen, one should expect a final mapping spatial resolution of close to 4 nm within such a configuration, provided the sample thickness at the point of beam incidence does not include superimposed crystals. An example of this resolution on a single silicon thin crystal presenting polytwinning is shown in the applications section.

The ability to reduce the beam broadening and, thus, improve the spatial resolution under precession is specific to the ASTAR technique that makes use of the ability to draw instrument-dependent compensation voltage curves for the Lower Beam Deflection coils in $x$ and $y$ direction, as can be seen in Figure 4.

Once the automated acquisition of several thousands of precessed diffraction patterns has been completed, phase and orientation identification is performed for each individual pattern, via comparison with previously generated model templates. These templates are kinematical electron diffraction patterns theoretically calculated for each crystallographic phase expected to be present in the sample.

With respect to the angular resolution obtained in the orientation maps, this depends on the angular grid used for the generation of the templates. A 0.8° interval is the default, and although a smaller sampling value is selectable, the final angular resolution – displayed as changing colours on the maps – will hardly show an improvement beyond this value, since spot diffraction patterns are insensitive to crystal tilts of less than 0.8°. Concerning acquisition times, for a typical 500 × 500 pixels map, beam scanning and precessing over the sample area will take around 5–15 min (200 points s$^{-1}$), typical mapped areas are of the order of 5 $\mu$m × 5 $\mu$m. Comparison with simulated templates can be done off-line and may take about 15 min for highly symmetric cubic materials but about three to six times longer for unit cells with lower symmetry as more templates must be generated.

The data processing software uses as input the collection of several thousand experimental diffraction patterns previously acquired. As a first step, the software produces transmitted beam intensity fluctuation maps (called virtual bright field images) by integrating the intensity within a virtual aperture placed on the same position for all the collection or block of acquired diffraction patterns, usually the centre of these. The resulting virtual bright field maps are helpful to recognize the scanned area of interest on the specimen and, moreover, when obtained under precessed illumination, are less sensitive to diffraction contrast and curvature effects, which makes
Fig. 4. Use of instrument-dependent compensation curves to obtain nanometre-size spatial resolution when using moderate-angle precession: the chosen focused beam size under precession is shown with distortion due to spherical aberration present even at less than 1° off-axis is shown in (A). Constant compensation curves along x- and y-axis are shown in (D), where the vertical axis is voltage amplitude and the horizontal axis is phase value. These curves are drawn and stored in order to turn the distortion shown in (B) into the resulting straight line in (C), both for x and y directions. The final result of both compensations is displayed in (E).

observation of features such as in-grain precipitates or stacking faults easier (Rebled et al., 2011). Complementarily, dark field images may be obtained as well by shifting the position of the virtual integrating aperture; this enables selective crystallite highlighting on the final virtual image.

Since each individual experimental pattern is compared with the full set of generated templates, a correlation index map (goodness of matching map) is obtained in association with the scanned area. This correlation index map emphasizes structural details such as precipitates and holes. A second quantitative map is also obtainable, since for each individual experimental pattern a specific best orientation is automatically chosen with an associated degree of confidence in the choice; this is called a reliability map and uses a similar principle to the confidence index in EDAX OIM software (Houge et al. US patent 6,577,970 B2, 2003), defined as

$$R = 100 \left(1 - \frac{Q_2}{Q_1}\right),$$

where $Q_1$ and $Q_2$ are the correlation indices for the selected first best solution and the second best. Reliability index decreases when more than one solution is possible for the diffraction pattern, so that reliability maps may clearly reveal grain and phase boundaries.

Strengths and limitations of the PACOM (ASTAR) technique

(1) Even at small magnifications, the maximum map size obtained is $15 \mu m \times 15 \mu m$, whereas EBSD can achieve map sizes of square millimetres.

(2) Standard ASTAR angular resolution is 0.8° but results of 0.2–0.5° can be achieved (Rauch et al., 2011). Kikuchi lines are more sensitive to small misorientations than spot diffraction patterns, allowing in standard mode, a resolution of 0.5°, but with new indexation algorithms resolutions of 0.01° are achievable (Wilkinson et al., 2006).

(3) Acquisition speed is an adaptable parameter in ASTAR – it can be chosen from 1 to 200 images s⁻¹, depending on the quality of the diffraction patterns acquired. Usually, between 50 and 100 images s⁻¹ are used as default settings. Due to the limited map size, this results in rapid acquisitions.

(4) ASTAR also allows easy phase recognition – even for crystals that exhibit the same symmetry – because the lattice parameter of the crystal is taken into account. However, it is estimated that a difference of more that 5% is necessary between two crystals of the same symmetry to give reliable results (Rauch et al., 2011). It is worth mentioning that a $6 \times 10^{-4}$ ultimate lattice resolution was achieved using nanobeam diffraction on a TEM by Beche et al. (2010). ASTAR may get quantitative results in terms of grain size applied to intensely plastically deformed specimens, for which EBSD is less adapted. This is discussed in the application examples section below. However, misorientation lower than 1° cannot be measured.

(5) As in EBSD-SEM technique, study of nonconducting samples can also be carried out with ASTAR, meaning that uncoated specimens can also be studied. Small thin particles deposited on grids do not have to be polished.

(6) The technique works particularly well with thin to relatively thick samples (a few nanometres to several hundreds of nanometres). For thicker samples, reliability maps are poor due to grain overlapping through the transmitted electron beam.

(7) The ASTAR unit may be adapted to several TEMs in the same laboratory and can be retrofitted from one microscope to another.

Applications

Although the tool was initially developed (Rauch & Dupuy, 2005) to deal with metallurgical samples subjected to severe plastic deformation, it has now been successfully applied to
a wide range of research subjects. A selection of examples is presented below.

**Grain orientation determination in metals/ alloys/ceramics**

ASTAR technique was initially developed to investigate materials subjected to severe plastic deformations, using equichannel angular pressing or compression-torsion techniques. Problems can arise when observation with EBSD techniques is carried out, because the Kikuchi lines used by different EBSD techniques (in TEM or SEM) are very sensitive to the crystal orientation and they rapidly disappear if the diffracting volume suffers distortions induced by high dislocation densities. Actually, this shortcoming was used as an advantage to measure volume fractions of recrystallized areas with EBSD in deformed materials (e.g., Tarasiuk et al., 2002). The first grain size measurement, following equichannel angular pressing or compression-torsion deformations, was carried out using ASTAR (Rauch & Dupuy, 2005).

By contrast with Kikuchi lines, the distortions due to high dislocation densities will have a limited effect on the spot patterns because small misorientations will affect the intensities of the diffracting beams, not their position. This results in a less accurate misorientation measurement (>1°) but usable diffraction patterns are nevertheless available to analyze. Effectively, it may be underlined that strains do not affect the capability of the tool to provide reliable information, i.e. orientation maps, grain size and crystallographic texture (Ignat et al., 2009). Figure 5 is a typical orientation map of a heavily deformed Titanium alloy. (Experimental conditions: TEM Tecnai F20; map pixel size, 15 nm; scanned area: 3 μm × 3 μm.)

Although EBSD-SEM tools are very efficient in deriving orientation maps with impressive spatial and angular resolution when coupled to an FEG-SEM, they still experience difficulties when the level of plastic strain in metals is significantly increased.

Nanocrystalline metals and alloys exhibit outstanding mechanical properties, in particular superior hardness and strength as well as fatigue properties, compared to their coarse-grained counterparts. For these ultrathin grained metals, modified or even new deformation mechanisms are expected to dominate the mechanical properties. Consequently, it will be important to characterize quantitatively and for different strain states features like the grain size distribution, local grain texture and twin density for metallic samples exhibiting grain sizes below 30–50 nm. For example, Weis et al. (2011) studied the deformation mechanisms in nanocrystalline palladium and palladium alloys by using mechanical testing in combination with ex situ and in situ TEM analysis and ASTAR. In addition, Descartes et al. (2011) obtained grain refinement by applying high-pressure torsion to pure iron and used the ASTAR to characterize the resulting fine-grained structure after this plastic deformation.

Using PED may greatly increase the quality of orientation/phase maps as the experimental PED patterns contain much more diffraction information: when compared with theoretical templates, this can result in high-quality correlation indices. Most importantly, without precession, the intensities of the excited reflections would not correlate to the square modulus of the structure factors of the considered crystals. In fact, the higher the precession angle, the higher the resemblance, but at the cost of loosing spatial resolution in the map, as the sharpness of the focalized beam gets lower (Rauch et al., 2010b), consequently, a balance between the two is needed. Figure 6 shows how a small precession angle of 0.5° enhances the quality of the patterns for Al2O3 polycrystal materials: when precession is used, grains are correctly indexed. (Experimental conditions: TEM Tecnai F20; map pixel size, 20 nm; scanned area, 2 μm × 2 μm.)

**Texture determination in rapidly solidified alloys**

In order to observe rapid solidification dynamics in 80-nm-thick Al thin films after pulsed laser melting, Kulovits et al. (2011) carried out studies using high-time resolution TEM. The nanometre spatial and 15 ns temporal resolutions of the dynamic TEM allowed them to study the morphology and dynamics of the transformation front moving at speed of 0.1–10 m s⁻¹ during rapid solidification. The posttransformation analysis of grain orientations for the solidified microstructure near the position of the solid–liquid interface at the start of solidification was only possible with the use of the automated precession diffraction tool.

Lagrange et al. (2011) used automated orientation indexing technique to study an exotic Cu microstructure developed...
Fig. 6. ASTAR orientation map on Al$_2$O$_3$ sample (crystal structure: trigonal, R3c; $a = 4.78$ Å, $c = 12.99$ Å) without using precession (A) and using a small precession angle (B), note the improvement on the orientation reliability. (Courtesy of M. Cantoni, EPFL, Lausane; Jeol 2200 FS and S. Lartigue, ICM-CNRS, Thiais, Paris.)

Fig. 7. ASTAR orientation and phase map in a transformation-induced plasticity – 304 steel. Austenite is represented in green in the phase map. Martensite is represented by two different phases in the sample; $\varepsilon$ martensite in blue and cubic martensite in red. (Courtesy of Dr. Ali Gholinia, University of Manchester, United Kingdom; CM 20 LaB$_6$.)

by pulsed, high-power sputter deposition. The growth mode under pulsed deposition develops columnar grains with large aspect ratio that contain a high density of fine twins oriented parallel to the substrate in the plane of the film. ASTAR was used to map changes in grain orientation and grain boundary area fractions using high-resolution maps of 1000 × 1000 pixels.

**TEM phase and orientation mapping in metals and alloys**

Wang et al. (2011) have studied forced chemical mixing in nanostructured Ag$_{60}$Cu$_{40}$ eutectic alloys during severe plastic deformation carried by high-pressure torsion that enables quantitative measurement of the processing variables. ASTAR was used to evaluate structural evolution of phases, compositions and grain shape, size and orientation. Rauch et al. (2012) have used the EBSD-TEM-like technique to analyze texture and phase distribution of ferritic/austenitic (also containing martensitic hexagonal phase) industrial steel and obtained an accurate phase/orientation analysis for a ferrite/austenite steel containing $\varepsilon$ martensite. Similar analysis have been carried out (Rauch et al., 2010a) in transformation-induced plasticity ferritic steel containing a small volume fraction of austenite. In that work, ASTAR PED-based crystal phase maps show, as expected, that the retained austenite is only found at the grain boundaries while observation based on data...
collected without precession gave misindexed austenite ‘inclusions’ within ferritic grains. This result is to be related to the dramatic improvement in the diffraction pattern quality with precession mentioned above.

Recent work on transformation-induced plasticity steels with ASTAR (Fig. 7) showed clearly 10 nm cubic martensite grains within a layer of ε martensite embedded in an austenitic matrix. (Experimental conditions: TEM CM 200; map pixel size, 20 nm; scanned area, 4 μm × 4 μm.)

Cizek et al. (2011) applied TEM-automated orientation indexing facility to analyze micro- and mesoscale crystallographic textures in electrodeposits of nanocrystalline Ni, Ni-20% Fe and Ni-50% Fe. In these samples, nanosized grains were arranged in coarse mesoscale colonies. In the as-deposited state, the bulk texture of the Ni-20% Fe alloy displays a dominant <0 0 1 > fibre parallel to the macroscopic deposition direction. The grains are elongated along the <0 0 1 > crystal lattice direction, which is mostly parallel to the local deposition direction, producing a well-defined <0 0 1 >/deposition direction fibre microtexture on a local scale.

**TEM phase and orientation mapping in nanoparticles and nanowires**

Nanoparticles have been a hot topic in several different fields for their astonishing and unusual properties compared to bulk materials and are still being investigated using *in situ* devices (Wang et al., 2012). New sciences like nanochemistry, nanomedicine and nanotoxicology have been born and an accurate knowledge of the nanoparticle structure is required to properly model their useful properties. Among these, the grain size, the defects and the particle shape are of major importance, since they easily correlate especially with optical properties. The knowledge of the grain size of nanoparticles can be easily obtained with conventional TEM techniques, but the coherent domains – those inside which the structure is defect-free (no twinning or grain boundaries) – are much more difficult to recognize and measure. The nanoparticle shape is another important factor to be known, since it drives the self-assembly. Examples of EBSD analysis of nanowires can be found in literature (Motayed et al., 2007; Vaudin et al., 2007) showing the potential of the technique. In Figure 8, we show an orientation map obtained on NaYF₄ nanoparticles. These nanoparticles are known as upconverting, since they are able to emit visible and near-infrared light when excited with near-infrared radiation. They are of great promise as fluorescent targets for their astonishing and unusual properties compared to bulk materials and are still being investigated using *in situ* devices (Wang et al., 2012). New sciences like nanochemistry, nanomedicine and nanotoxicology have been born and an accurate knowledge of the nanoparticle structure is required to properly model their useful properties. Among these, the grain size, the defects and the particle shape are of major importance, since they easily correlate especially with optical properties. The knowledge of the grain size of nanoparticles can be easily obtained with conventional TEM techniques, but the coherent domains – those inside which the structure is defect-free (no twinning or grain boundaries) – are much more difficult to recognize and measure. The nanoparticle shape is another important factor to be known, since it drives the self-assembly. Examples of EBSD analysis of nanowires can be found in literature (Motayed et al., 2007; Vaudin et al., 2007) showing the potential of the technique. In Figure 8, we show an orientation map obtained on NaYF₄ nanoparticles. These nanoparticles are known as upconverting, since they are able to emit visible and near-infrared light when excited with near-infrared radiation. They are of great promise as fluorescent targets for biological imaging. NaYF₄ crystallizes in two forms: one cubic and one hexagonal. ASTAR was able to make the crystal identification. Those particles having hexagonal shape are oriented with the c-axis (the 6-fold axis) normal to the plane, while those that are rectangular are oriented with the c axis parallel to the plane. This indicates that a spatial resolution of a few nanometres can be obtained on a TEM-FEG microscope coupled to ASTAR, making it a tool well adapted for orientation/phase mappings in nanoparticles. Rouvimov et al. (2009) have successfully used ASTAR to distinguish phases out of a mixture of iron oxide nanocrystals (magnetite and maghemite), which have essentially similar cubic cell parameters but different space group symmetries. M. Gemmi (private communication) used a 120 kV Libra 120 TEM to discriminate orientations in Au nanoparticles as small as 20 nm and analyze FeₓOᵧ nanoparticles used as drug delivery compound. This showed that the nanoparticles were hexagonal prisms with a height comparable with the base sides. (Experimental conditions: TEM Zeiss Libra 120; map pixel size, 3 nm; scanned area: 0.7 μm × 0.7 μm.)

Another study was carried out by Estrade et al. (2012). They have used ASTAR to determine crystal orientation changes in 50-nm-thick Phosphorous containing Cobalt nanowires and in heavily bent Germanium nanowires, only 10-nm-thick. The technique allows the determination of the nanowires orientation, its degree of polycrystallinity and the orientation of the different grains within the nanowire when a polycrystalline state exists. The z, x and y orientation maps (multiplied by index map) of Ge nanowires are displayed in Figure 9. It may be noted that the crystal orientation changes after the second bending point, but not after the first one.

©2013 The Authors. *Journal of Microscopy* published by John Wiley & Sons Ltd on behalf of Royal Microscopical Society, 252, 23–34
The use of precession for the 50-nm-thick metallic wire, even with a precession angle as low as 0.6°, is all-important. Without precession, there would be a contribution of Kikuchi lines to the pattern (Kikuchi lines disappear when working with precession angles > 0.5°). In the case of the 10-nm-thick semiconductor nanowires, the use of precession is only slightly improving the correlation index maps as compared to mapping the same area without precession. This is due to the already extremely thin nature of the nanowires.

Fig. 9. Ge nanowires orientation maps: (A) z-axis; (D) y-axis; (C) x-axis; (multiplied by index map [b]).

Brandstetter et al. (2010) also performed an intensive TEM-ASTAR orientation analysis study of pattern size dependence of grain growth in Cu interconnects. The same group analyzed Cu–Cu interface bonding by interdiffusion of copper and using the integrated mapping tool, they emphasized the grain growth from one layer to the other.

Häusler et al. (2011) studied crystallite phase and orientation determinations of (Mn, Ga) As/GaAs crystals using ASTAR PED patterns. (Mn, Ga, As) crystallites may have monoclinic, hexagonal, orthorhombic and trigonal phases, which are embedded as precipitates into the GaAs matrix. Using PED and template matching for all the above mentioned phases (more than 38 000 templates in total), it was found that the precipitate crystal structure best matched the monoclinic P21/m phase.

Similarly, orientation of Al(Ga)N layers on patterned sapphire have been studied by Kirmse et al. (2012) and phase identification of both AlN and GaN crystals has been possible, revealing the sensitivity of the ASTAR technique to crystals having the same cell parameters but different chemical composition. These authors also studied polycrystalline ZnO and its orientation relationship with the C_{18}H_{18} sexiphenyl 6P, on which it is deposited. Due to completely divergent structural and chemical properties of ZnO and 6P, phases are not expected to be epitaxial, this was confirmed by automatic orientation analysis in a more effective and less tedious way than through HREM-TEM measurements (Kirmse et al., 2011).

TEM phase and orientation mapping in energy-related materials and thin films

An illustrative example of automated indexing used in combination with PED concerns energy-related materials and has been recently published by Brunetti et al. (2011). In his work, ASTAR was used to distinguish between LiFePO_{4} and FePO_{4} phases at the nanometre-scale level on a large number of particles whose sizes ranged between 50 and 300 nm in a partially charged battery. Despite the similarity of the two phases (the difference of lattice parameters is <5%), the method gives clear results that have been confirmed using high-resolution transmission electron microscopy and energy-filtered transmission electron microscopy/electron energy loss spectroscopy experiments. The phase maps show that the particles are either fully lithiated or fully delithiated and, therefore, strongly support the theory in which a domino-cascade process is operative at the nanoscale level (in those maps the experimental conditions used were: TEM Jeol 2010 FEG; spot size, 2.7 nm; step, 5 nm; scanned area 1 µm × 1 µm).

In another example, Rauch et al. (2011) used the ASTAR technique to analyze the texture of Pt, Cu and W thin films prepared by sputter deposition onto oxidized Si substrates.
Orientation maps in minerals

ASTAR has further been used for mineral orientation and phase identification. In the example shown in Figure 10, an ASTAR orientation map of heavily deformed olivine mineral is shown. The sample studied (which is beam-sensitive) is a forsterite (olivine containing Mg and not Fe) that has been synthesized in laboratory, applying high-pressure and high-temperature conditions using specific equipment (D-DIA) that simulates earth superior mantle conditions at 200–300 km

Fig. 10. Olivine area analyzed with ASTAR. (Courtesy of Dr. Caroline Bollinger and Dr. P. Cordier, University of Lille, France.)

Fig. 11. Polytwinned silicon grain displaying twin boundaries. Spatial resolution of 2 nm is reached and twin boundaries of 5 nm width are revealed.
depth where olivine is the majority phase. The sample formed with the D-DIA at 1373 K, 3 GPa and deformed at 40% is expected to contain an important number of structural defects. It should be noted that besides the high number of defects shown in the TEM bright field images, it was possible to map detail orientations with ASTAR and no information was possible to obtain with EBSD-SEM orientation mapping due to the highly strained areas present in this sample.

**Orientation mapping spatial resolution**

Nanometre-level poltwinning demands the best possible spatial resolution from a diffraction pattern recognition technique such as ASTAR. On FEG type microscopes, the attainable spatial resolution under precessed illumination is 1 nm (LaGrange et al., 2013), in the example above 2 nm spatial resolution is reached (Fig. 11). A poltwinning silicon grain displays twin boundaries of 5 nm width. Step width used in this measurement is 2.1 nm and the precessed illumination angle is 0.6°. Twinning is confirmed via the disorientation values measured at the boundaries, 60°. The orientation maps will only display the recognized twin boundaries when viewing the x and y projected orientation maps, since twinning appears on the diffraction patterns as double spots along specific directions perpendicular to the viewing direction.

**Future trends: phase and orientation mapping in organic crystals/beam-sensitive materials**

Orientation and phase mapping in organic crystals is one of the most promising areas for future developments for ASTAR technology. Organic crystals, or beam-sensitive materials in general, may still give orientation/phase information provided the specimen area is scanned at a sufficiently high speed to capture ED/PED patterns before irradiation damage may degrade them substantially. In the example shown in Figure 12, although the sample is damaged after beam scanning (time per acquisition 0.01 s), registered ED data allow to analyze particle orientation in detail. The information showed that fibres were indeed single crystals (in contrary to what has been assumed thus far) and they grow along a specific crystallographic direction. Veron et al. (2011) used ASTAR to reveal orienta-
tion mapping from an organic TRIS crystal (SG Pna21- unit cell 0.7768 nm × 0.8725 nm × 0.8855 nm C_{16}H_{46}N_{4}O_{12}) and demonstrated that it is possible to collect orientation information without relying on cryo-TEM techniques.
organic structures have revealed orientation information with ASTAR and the topic is clearly promising for future developments.

Conclusions

TEM-based orientation mapping (ASTAR) in combination with PED diffraction allows orientation and phase mapping in materials with spatial resolution down to 1 nm, opening new possibilities and fields of study with the TEM microscope. Samples from metals and ceramics or beam-sensitive organic crystals can be studied with any PED-ASTAR-coupled TEM microscope. Rapid acquisition time means that this technique is adequate for laboratory environments.

References

Barmak, K. (2010) Orientation Mapping in the Transmission Electron Microscope (OM-TEM), MRSEC Summer School of the Mesoscale Interface Mapping Project (MIMP), CMU, Pittsburgh.

Beche, A., Clement, I. & Rouviere, J.-L. (2010) Improved accuracy in nano beam electron diffraction. J. Phys. Conf. Series. 209(1), 012063.

Brandstetter, S., Rauch, E.F., Carreau, V., Maitrejean, V., Verdier, M. & Legros, M. (2010) Pattern size dependence of grain growth in Cu interconnects. Scripta Materialia. 63, 965–968.

Brunetti, G., Robert, D., Bayle-Guillemaud, P., Ignat, M., Lay, S., Roussel D’herbey, F., Seguineau, C., Malhaire, C. & Houge, E.C., Mcintosh, J.M., Plew, L.E., Stevie, F.A. & Vartyli, C. (2010) Confirmation of the domino-cascade model by LiFePO4/FePO4 precession electron diffraction. Chem. Mater. 23(20), 4515–4524.

Cho, J.-Y., Lee, H. J., Kim, H.N. & Sypunar, J.A. (2005) The effect of stress distribution on texture of Cu Damascene interconnects during annealing. Arch. Metall. Mater. 1, 256–266.

Cizek, P., Barnett, M.R., Nave, M.D., Rauch, E.F. & Balasubramaniam, R. (2011) Microscale and mesoscale crystallographic textures of nanocrystalline ni-based electrodeposited. Metall. Mater. Trans. A 42 7, 2048–2060.

Descartes, S., Desrayaud, C. & Rauch, E.F. (2011) Inhomogeneous microstructural evolution of pure iron during high-pressure torsion. Mater. Sci. Eng. A 528, 3666–3675.

Estrade, S., Portillo, J., Mendoza, J., Kosta, I., Serret, M., Müller, C. & Peiró, F. (2012) Assessment of misorientation in metallic and semiconducting nanowires using precession electron diffraction. Micron. 43(8), 910–915.

Ganesh, K.J., Rajasekhar, S., Bultreys, D., Zhou, P. & Ferreira, P.J. (2010) Automated local texture and stress analysis in Cu interconnects using DSTEM and precession microscopy. Microsc. Microanal. 16 (Suppl 2).

Häusler, I., Nicolopoulos, S., Rauch, E.F., Volz, K. & Moeck, P. (2011) Crystallite phase and orientation determinations of MnGaAs/GaAs crystallography using analyzed (precession) electron diffraction patterns. In Proceedings of the Microscopy Conference (MC 2011). August 28–September 2, 2011, Kiel, Germany.

Houge, E.C., McIntosh, J.M., Plew, L.E., Stevie, F.A. & Vartyli, C. Method of Determining a Crystallographic Quality of a Material Located on a Substrate. Agere Systeme Inc., US Patent 6,779,790.

Ignat, M., Lay, S., Roussel D’Herbey, F., Seguineau, C., Malhaire, C. & Desmarres, J.M. (2009) Micro tensile tests on aluminium thin films: tensile device and in situ observations. Mater. Res. Soc. Symp. Proc. 1139, doi: http://dx.doi.org/10.1557/PROC-1139-GG04-04.

Keller, R.R. & Geiss, R.H. (2011) Transmission EBSD from 10 nm domains in a scanning electron microscope. J. Microsc. 245, 245–251.

Kim, D., Paik, J., Joo, Y., Oh, K.H., Lee, H. & Dicks, K. (2002) Microtexture measurement of copper damascene line with EBSD. Mater. Sci. Forum. 408, 529–534.

Kirmse, H., Häusler, I., Nicolopoulos, S., Blumstengel, S., Sadojčí, S. & Henneberger, F. (2011) Texture analysis of nanocrystalline ZnO by scanning nanobeam diffraction. In Proceedings of the Microscopy Conference (MC2011). August 28–September 2, 2011, Kiel, Germany.

Kirmse, H., Häusler, I. & Mogilantenko, A. (2012) ASTAR applications for semiconductor materials (2012) ADT-ASTAR Workshop. March 19–29, 2012, KIT Karlsruhe, Germany.

Kulovits, A., Wizioerek, J.M.K., Lagrange, T., Reed, B.W. & Campbell, G. (2011) Revealing the transient states of rapid solidification in aluminum thin films using ultrafast in situ transmission electron microscopy. Philos. Mag. Lett. 91(4), 287–296.

Lagrange, T., Reed, B.W., Wall, M., Mason, J. & Barbee, T. (2013) Topological view of the thermal stability of nanotwinned copper. Appl. Phys. Lett. 102, 011906.

Rauch, E.F. (2008) Microsc. Anal. 9(85).

Rauch, E.F. & Dupuy, L. (2005) Rapid diffraction patterns identification through template matching. Arch. Metall. Mater. 50, 87–99.

Rauch, E.F., Portillo, J., Nicolopoulos, S., Bultreys, D., Rouvimov, S. & Moeck, P. (2010a) Automated nanocrystal orientation and phase mapping in the transmission electron microscope on the basis of precession electron diffraction. Zeitschrift für Kristallographie (Precession Electron Crystallography). 225(2–3), 103–109.

Rauch, E.F., Portillo, J., Nicolopoulos, S., Bultreys, D., Rouvimov, S. & Moeck, P. (2010b) Automated nanocrystal orientation and phase mapping in the transmission electron microscope on the basis of precession electron diffraction. Zeitschrift für Kristallographie. 225, 103–109.

Rauch, E.F., Barmak, K., Ganesh, J.K., et al. (2011) Automated crystal orientation and phase mapping for thin film applications by transmission electron microscopy. Microsc. Microanal. 17, 1086–1087.

Rauch, E.F., Veron, M., Nicolopoulos, S. & Bultreys, D. (2012) Orientation and phase mapping in TEM microscopy (EBSD-TEM like): applications to materials science. Solid State Phenom. 186, 11–15.

Rebled, J.M., Yedra, L.L., Estrade, S., Portillo, J., Peiro, F. (2011) A new approach for 3D reconstruction from bright field TEM imaging: beam precession assisted electron tomography. Ultramicroscopy. 111(9–11), 1504–1511.

Rouvimov, S., Rauch, E.F., Moeck, P. & Nicolopoulos, S. (2009) Automated crystal orientation and phase mapping of iron oxide nanocrystals in a transmission electron microscope. Microsc. Microanal. 15, 1290–1291.

Tarasiuk, J., Gerber, P.H. & Bacroix, B. (2002) Estimation of recrystallized volume fraction from EBSD data. Acta Materialia. 50, 1467–1477.
Trimby, P.W. (2012) Orientation mapping of nanostructured materials using transmission Kikuchi diffraction in the scanning electron microscope. Ultramicroscopy, 120, 16–24.
Vaudin, M.D., Motayed, A. & Sundaresan, S.G. (2007) Crystal structure and orientation determined by EBSD. Microsc. Microanal. 13(Suppl 2), 936–937.
Veron, M., Rauch, E.F., Nicolopoulos, S., Li Ling, W. & Otero, J.M. (2011) Novel electron diffraction technique for texture analysis (orientation & phase mapping) of organic nanocrystals PXRD 10. In Proceedings of the Workshop for Pharmaceutical Applications., International Centre for Diffraction Data, Lyon, France.
Vincent, R. & Midgley, P. (1994) Double conical beam rocking system for measurement of integrated electron diffraction intensities. Ultramicroscopy, 53, 271–282.
Wang, D., Pouryazdan, M., Scherer, T., Kübel, C. & Hahn, H. (2011) Structural evolution during forced chemical mixing of an immiscible Ag-Cu nanocomposite. In Proceedings of the Microscopy Conference (MC2011), August 28–September 2, 2011, Kiel, Germany.
Wang, Z., Mook, W.M., Niederberger, C., Ghisleni, R., Philippe, L. & Michler, J. (2012) Compression of nanowires using a flat indenter: elasticity measurement in nanoscale. Nano Lett. 12(5), 2289–2293.
Weis, A., Castrup, A., Kübel, C. & Hahn, H. (2011) Quantitative evaluation of the structure of bulk nanocrystalline Pd by orientation imaging in TEM. In Proceedings of the Microscopy Conference (MC2011), August 28–September 2, Kiel, Germany.
Wilkinson, A.J., Meaden, G., & Dingley, D.J. (2006) High resolution mapping of strains and rotations using electron backscatter diffraction. Mater. Sci. Technol. 22(11), 1271–1278.
Zuefler, S. (2011) A critical review of orientation microscopy in SEM and TEM. Cryst. Res. Technol. 46(6), 607–628.