esteem 2
european network for electron microscopy

FP7-INFRASTRUCTURES-2012-1

Enabling Science and Technology through European Electron Microscopy

Project Acronym: ESTEEM2
Grant Agreement n°: 312483

Final Scientific Report
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Acronyms list

Consortium partners	
CNRS	Centre National de la Recherche Scientifique
UOXF	The Chancellor, masters and scholars of the University of Oxford
UA	Universiteit Antwerpen
Cambridge	The Chancellor, masters and scholars of the University of Cambridge
Jülich	Forschungszentrum Jülich Gmbh
MPG	Max Planck Gesellschaft zur Foerderung der Wissenschaften e.v.
TU Delft	Technische Universitet Delft
Chalmers TH	Chalmers Tekniska Hoegskola AB
TU Graz	Technische Universität Graz
UCA	Universidad de Cadiz
UNIZAR	Universidad de Zaragoza
JSI	Institut Jozef Stefan
AGH	Akademia Gorniczo-Hutnicza im. Stanislawa Staszica w Krakovie
TUD	Technische Universität Dresden
Nanomegas	Nanomegas SPRL
CEOS	CEOS Corrected Electron Optical Systems Gmbh
Infrastructure integrated acronyms	
JRA	Joint Research Activity
NA	Networking Activity
TA	Transnational Access
RP	Reporting Period
Electron Microscopy techniques acronyms	
ABF / ADF	Annular Bright Field / Annular Dark Field
CCD	Charge Cumulative Detector
CL	Cathodoluminescence
DFT	Discrete Fourier Transform
EDS / EDX	Energy-Dispersive X-ray Spectroscopy
EELS	Electron Energy Loss Microscopy
EFTEM	Energy-Filtered Transmission Electron Microscopy
EH	Electron Holography
EMCD	Electron Magnetism Circular Dichroism
FEBID	Focused Electron Beam Ion Deposition
FIB	Focussed Ion Beam
HAADF	High-Angle Annular Dark-Field imaging
HREM / HRTEM	High-Resolution (Transmission) Electron Microscopy
MRFM	Magnetic Resonance Force Microscopy
SEM	Scanning Electron Microscope
SPET	Scanning Precession Electron Tomography
STEM	Scanning Transmission Electron Microscope
STM	Scanning Tunnelling Microscope
TEM	Transmission Electron Microscope

1) Executive Summary

The ESTEEM2 integrating initiative in advanced electron microscopy for the physical sciences brings together the leading European Laboratories in this field in a sustainable network. This network represents an EU group with critical mass in the wide range of techniques available for materials characterisation using electrons. Within ESTEEM2 the partners have provided free transnational access to state of the art instrumentation, they have participated in networking activities designed to improve access and strengthen links within the EU academic and industrial sectors, and they have undertaken collaborative research programs aimed at further developing advanced EM techniques.

The core of the ESTEEM2 activities has been the provision of Transnational Access (TA) to state of the art instruments located in the partner laboratories. The instrumentation provided represents differentiated state of the art TEM columns, optimized for specific experiments and advanced sample preparation and data analysis facilities. Through the TA mechanism we have enabled new collaborative science with research groups from a wide range of disciplines who would otherwise not have access to the level of instrumentation provided by ESTEEM2. In four years, ESTEEM2 has offered 3669 access days to international users from across Europe.

The network activities (NA) firstly aimed at disseminating the outputs of ESTEEM2 to both academic and industrial users and the wider media. An important component of this activity has been the organisation of a series of workshops offering training by specialists in advanced techniques. Thirteen schools and workshops were organised within ESTEEM2, attended by 600 participants. The second set of network activities has developed the core tools required to provide a stable pan-European user facility across multiple laboratories. In particular, ESTEEM2 has developed 25 protocols for sample preparation and for specific experimental methods and has provided 15 software to enable users to analyse and interpret their data. These protocols and software are provided in an open-access format on the ESTEEM2 website.

The Joint Research Activities (JRA) concentrated on advancing four established key EM methodologies; diffraction, imaging, spectroscopy, and 3D nanometrology together with projects in the emerging field of time resolved experiments using electrons. Outstanding results were obtained in the following example areas:

- crystallographic studies of a wide range of organic, inorganic and metal/alloy materials
- the development of new imaging methods that more precise information about the sample
- deep understanding of plasmon physics and their interaction with electrons
- precise and quantitative 3D measurements of the structure and properties of nanomaterials at the atomic scale
- the prototype construction of an ultrafast CFEG TEM that will be of great importance for the local study of ultrafast dynamical processes at the nanoscale.

The pioneering work in these activities is likely to see significant impact in many areas of materials science, including new materials for clean energy, functional magnetic materials, multiferroic materials, improved alloys and coatings for aerospace and automotive industry, nano-oxides, fundamental properties of spintronics / ferroelectrics, and nano-crystalline metals. In turn these have direct relevance to key industrial and applied technologies for example, within the European microelectronics industry, in storage media, telecommunications, renewable energy sources, environmental protection, and biomedicine.

2) Summary description of project context and objectives

The main objective of the ESTEEM2 integrating initiative on advanced electron microscopy in materials science was to create a sustainable framework for the consolidation of European critical mass in characterization using electrons. The ESTEEM2 project started in September 2012 within the European call: "*INFRA-2012-1.1.22. Imaging, Diffraction and Spectroscopy using Electrons*" and was organized to address the EC request: "*A project under this topic should integrate key facilities and state-of-the-art technologies in the field of electron-based analytical approaches*".

In 2012, ESTEEM2 was supported as the follow-up to the previous "ESTEEM" Integrated Infrastructure Initiative (I3, 2006-2011) of the FP6. These two successive ESTEEM and ESTEEM2 projects were established as the primary European portal for users who need access to state of the art TEM instrumentation, methodology or tools.

For the creation of the ESTEEM2 consortium fifteen academic partners with expertise in advanced TEM techniques and covering a large geographical area across Europe (Toulouse, Orsay, Oxford, Cambridge, Antwerp, Stuttgart, Dresden, Julich, Delft, Chalmers, Graz, Krakow, Cadiz, Zaragoza and Ljubljana) combined their efforts for the development of Electron Microscopy in Europe. Two SMEs (CEOS and Nanomegas) were also part of the ESTEEM2 consortium and both were directly involved in the development of commercial ancillary instrument design and manufacture. All partners have the latest generation of TEM instruments available for unique experiments in EELS, HR(S)TEM, Holography, Tomography, Diffraction and *in-situ* microscopy at the sub 100pm level and with exceptional energy resolution. In addition, several partners in the infrastructure own advanced FIB and sample preparation tools for essential for state of the art TEM specimen preparation.

With this consortium **ESTEEM2 was able to reach its objective to provide TEM service provision for the industrial and academic communities in Europe and to offer access to the most powerful TEM instruments and characterization techniques available for solving complex materials.** We have set up a transparent, simple peer review process based on merit and scientific priorities through which we offer Transnational Access (TA) to appropriate TEM instruments in the consortium. The TA funding scheme was structured to cover the full running cost of the experiments on the selected microscopes (making access free at point of use) but also, if needed and requested by the user, sample preparation, data analysis, and travel and lodging costs for the user(s). A typical TA project lasted from a few days to a few weeks depending of the nature of the experiments.

The seventeen ESTEEM2 partners are involved in different and complementary fields of electron microscopy and were selected to create significant added scientific value. **However, the benefit of this complementary partner expertise required that the ESTEEM2 research infrastructures operate, evolve and interact with each other and with users to form an efficient collaborating network**. To achieve this a series of five Networking Activities (NAs) have been established to support an optimal integration between the different users and partners.

The first NA (WP2) activity was focused on the organization of workshops and schools that disseminate cutting-edge TEM techniques. This WP2 enabled new users to become familiar with a range of innovative EM capabilities offered through TA in ESTEEM2. These workshops and schools covered a wide range of TEM techniques including advanced sample preparation procedures, state of the art spectroscopy (EELS, EDX) ultra-high resolution imaging (HREM, HRSTEM-HAADF), electron holography, and electron tomography among others. These training sessions were planned so that European scientists could take best advantage of TA access within ESTEEM2.

The second NA (WP3) aimed at optimizing methods for preparing thin and representative TEM lamellae extracted from a wide range of modern materials and devices from academic and industrial worlds. One of the WP3 objectives was to create a library of standards describing optimum specimen preparations that will be disseminated as an EU

reference document. It also provided essential support and service to TA users by ensuring that they could have access to suitable sample preparation methods.

In the third NA (WP4), several ESTEEM2 partners have worked to create standard distributed models and computational tools related to different TEM methods including imaging, spectroscopy and tomographic reconstruction. This NA also acted as a central point for access to "open access software" in support of service provision for free download from the ESTEEM2 website (www.esteem2.eu).

Closely related to WP3 and WP4, a dedicated "Advanced Service Provisions" (WP6) was established to drive developments in ESTEEM2 toward the users need for advanced TEM capabilities and tools and to facilitate the transfer of deliverables developed in other activities. Users and partners have access to developments within ESTEEM2 via the project website, where they can find and download specialized sample preparation recipes, software, scripts, experimental protocols and lecture notes.

To ensure the promotion of ESTEEM2 capabilities to the industrial and academic communities in Europe, a final NA (WP5) was created with responsibility for professional publication and dissemination of the project in a coordinated manner. This NA was also tasked with stimulating connections between ESTEEM2 and other national and international TEM programs in order to promote a wider global coordination in TEM. One of the WP5 tasks was to establish the sustainability of the framework to ensure the consolidation of European critical mass in EM, in particular through coordination with national agencies.

The ESTEEM2 project also aimed to optimize state-of-the-art TEM instruments available in Europe and to develop new advanced TEM methods for the benefit of users and more generally of European scientists. The consortium has decided to put its main research effort in the development of key advanced quantitative TEM methods required to solve relevant questions in materials and nano-science within five Joint Research Activities (JRAs). In turn, these have supported disruptive scientific and technological developments in EM advanced methods. Specifically, the following five JRAs were designed to provide a higher level of overall user service provision and to strengthen TA capabilities within the consortium.

The first JRA "**Diffraction**" (WP20) aimed at advancing electron diffraction-based methods for solving structures at the nanometre scale using electrons. The main target was to develop methods to extract reliable quantitative information from the refinement of reflection intensities obtained in precession electron diffraction to determine the 3D optimum structure of unknown crystalline phases at the nanometre scale. A specific task has focused on experimental methods for the mapping of 2D and 3D crystallographic orientation in polycrystalline materials. Another specific target of this JRA was to develop a unique approach for the study of lattice vibrations from analysis of diffraction patterns. This JRA involved academic partners and benefited from the expertise of the SME *Nanomegas* in developing tools for local quantitative electron diffraction methods.

The second JRA "**Imaging**" (WP21) focused on quantitative imaging using TEM (both HRTEM and HRSTEM-HAADF) at sub 100pm resolution using the most advanced Cs corrected microscopes along with the development of innovative methods to process the data. The work involved both the development of new procedures to be added to the capabilities within ESTEEM2, and an exploration of which imaging modes can provide the most useful information for a particular sample type. A particular task was the study of different detectors geometries in STEM. Dedicated tasks related to new modes for imaging and the development of advanced codes for the improvements of the match between simulation and experiment were also undertaken.

The third JRA "**Electron Spectroscopy**" (WP22) focused on the development of advanced electron spectroscopy methods and procedures for the local measurements of magnetic, electronic and optical properties. It involved the use of dedicated TEM and STEM instruments available within the ESTEEM2 consortium, the development of new

tools (including beam shaping) and new procedures to extract reliable physical parameters related to magnetism, optics and electronic structure at the nanometre scale. In addition, an additional activity was added on the development of quantitative, atomically resolved EELS and EDX.

The fourth JRA (WP23) focused on the developments required to provide 3D information as current technology led demand requires the quantitative measurement of 3D properties including chemical composition, magnetic fields and strain distributions. This JRA combined three different TEM methods (tomography, holography and confocal microscopy) to advance "**3D nanometrology**" of structures and fields. This required the development of new tomographic methods and reconstruction algorithms for the 3D reconstruction of structures at the atomic scale as well as procedures to perform 3D mapping of electromagnetic fields using electron holography and the design and application of new sample holders.

The last JRA "**Time resolved microscopy**" (WP24) was different from the previous ones, as it was an instrumental activity requiring important design and manufacturing. This JRA aimed at stimulating progress in Europe in time-resolved TEM experiments, which were not available at the beginning of the project. Two time scales were targeted: the millisecond to second regime, which required the development of novel fast (direct) detectors and the pico-second to nanosecond regime. The later necessitated the development of an innovative and tunable electron gun able to generate a coherent laser-driven pulsed electron beam (the probe) and of a peculiar set-up allowing a laser pulse to be sent to the studied sample (the pump) located in the TEM goniometer to perform pump-probe experiments.

3) Description of the main scientific and technical results / foreground

Work Package 2: TEM schools, advanced training sessions and workshops

This activity focused on training in the recent and future developments in quantitative TEM for nano-materials science. The goal of this activity was to spread knowledge to a range of participant levels in advanced techniques related to TEM. Specific objectives were to offer schools and advanced workshops to microscopists in order to enable them to exploit the new possibilities in TEM. Six schools and seven advanced workshops were successfully organized within ESTEEM2 and were open to the European research community (academia, research institutes and industry) with free access for ESTEEM2 members. This networking activity was further separated into two main tasks:

Task 2.1: TEM Schools

Task 2.1 involved in the organization of schools to transfer knowledge about TEM techniques aimed at postgraduate scientists in the early stages of their careers. The following schools were successfully organized within this task:

- 2 EMAT Winter Schools (UA – 91 attendees in total)
- 1 TEM-UCA Summer School (UCA – 21 attendees)
- 1 European School on TEM Basics (AGH – 35 attendees)
- 1 European School on Advanced TEM Sample Preparation (MPG – 22 attendees)
- 1 European School on Advanced Quantitative TEM Measurement Techniques - QEM2013 (CNRS-CEMES – 95 attendees)

In total, 264 participants attended the ESTEEM2 schools.

Task 2.2: Advanced training sessions and workshops

Task 2.2 involved the organization of dedicated training sessions and workshops focused on specific advanced TEM technique as follows:

- HRTEM and Holography (TU Dreden – 58 attendees)
- Spatially-resolved electron spectroscopy (TU Graz – 59 attendees)
- Principles and Applications of Aberration-Corrected imaging (UOXF – 31 attendees)
- Electron Crystallography (UCAM – 38 attendees)
- Quantitative (S)TEM Imaging and EELS (JSI – 35 attendees)
- In situ and environmental TEM (Chalmers TH – 89 attendees)
- 3D Methods (UA – 26 attendees)

In total, 336 participants attended the ESTEEM2 workshops.

Significant results

- In total, 600 participants have benefited from the ESTEEM2 workshops and schools
- Two workshops, one symposium and one summer school were additionally organized by the members of the consortium

Work Package 3: Optimizing EM Sample Preparation

The most widely used techniques for the preparation of thin foil specimen from various materials for Transmission Electron Microscopy observation include ion milling, FIB technique, tripod polishing, electro-polishing and ultramicrotomy. With the introduction of a new generation state-of-the-art aberration (Cs, Cc) corrected TEM/STEMs, the need for optimized and/or new approaches for preparation of high quality artefact-free samples with even thickness, large field of view, with no amorphous layer and no contamination during observation has dramatically increased. Although thin foil specimen preparation is routinely performed in every electron microscopy laboratory there have been only few systematic studies on optimization of sample preparation techniques and new techniques that would yield standardized sample preparation procedures that would be verified by different electron microscopy laboratories.

Task 3.1: Optimization of TEM Sample Preparation:

Standard methods for thin foil specimen preparation, such as tripod polishing, ion milling, FIB techniques, electro-polishing and ultramicrotomy were optimized in respect to operation procedures and implemented on many technologically important materials (Si-based semiconductors, layered three-dimensional topological insulators, SiC fibres, perovskite nanorods and nanotubes, platelet crystals, Ni-based alloys, biological samples, organic/inorganic composites). Special attention was given to optimization of FIB prepared samples in order to minimize ion implantation artefacts.

Task 3.2: Standardization of Preparation Procedures:

Two Round Robin Tests were conducted in order to determine the reproducibility of sample preparation when using same materials and same preparation recipes in different electron microscopy laboratories. A general conclusion is that specimen preparation by FIB results in similar quality specimens when prepared in different laboratories. The specimen's quality shows wider variation in the case of tripod polished and ion-milled specimens and even more in the case of electropolishing.

Task 3.3: New Sample Preparation Techniques:

New sample preparation techniques included studies of low-energy ion milling with the aim to determine conditions to minimize the thickness of amorphous layers as well as to minimize sample contamination during STEM investigations. Low temperature FIB and new approaches for the preparation of needles for tomography observations using FIB were also implemented.

Significant results:

- Twenty-four published protocols on specimen preparation on the ESTEEM2 website.
- Twenty-two publications related to thin foil specimen preparation and more than fifty publications generally related to Work Package 3
- New FIB approaches for preparation of thin foil specimens as well as needles for tomography observation.

Work Package 4: Theory

Prior to the start of ESTEEM 2 there was limited data that critically compared exit wavefunction reconstruction methods in a quantitative fashion. In addition, all previously reported methods required multiple image datasets. There have also been breakthroughs in combined electron/optical spectroscopy techniques such as Electron Energy Gain Spectroscopy, a method not established at the start of ESTEEM2.

Task 4.1: Spectroscopic Calculations

Task 4.1.1 First principles DFT calculations.

The type and distribution of oxygen functional groups in Graphene oxide (GO) and Reduced Graphene Oxide (RGO) are a subject of great debate. To address these questions, local analytic techniques are required to access the local nm scale chemistry of these materials. Electron Energy Loss Spectroscopy (EELS) in a Scanning Transmission Electron Microscope (STEM) can provide suitable resolution, but GO and RGO are extremely sensitive to electron irradiation. GO oxygen maps have been obtained showing well separated domains with a C over O ratio of about 4 and 1, the latter corresponding to complete functionalization of the graphene flake. In RGO the residual oxygen is also mostly concentrated in regions of a few 10's of nm. Specific Energy-Loss Near-Edge Structures (ELNES) are observed for different oxidation levels. First principles simulations have been extensively developed and we have used these to build a model for the highly-oxidized domains where graphene is fully functionalized by hydroxyl groups forming a 2D sp3 carbon network analogous to that of graphene.

Task 4.1.2 Numerical Simulations of plasmonic systems.

In this task there have been several breakthroughs in combined electron/optical spectroscopy techniques such as Electron Energy Gain Spectroscopy (PINEM). CEMES-CNRS has developed EELS-GDM, a numerical framework to describe these advanced spectroscopies and anticipate experiments to be performed in the framework of WP24 (ultrafast TEM). These describe the interaction of fast electrons with metallic nanostructures based on the 3D Green Dyadic Method. Figure 4.1 shows a map of the PINEM signal from a dimer of proximal silver nanoparticles and the gain probability computed from first order perturbation theory using the *EELS-GDM* framework. In the case of high power optical excitation, higher order interactions develop between the optical field and the free electrons yielding more complex dynamics characterized by multiple photon sidebands.

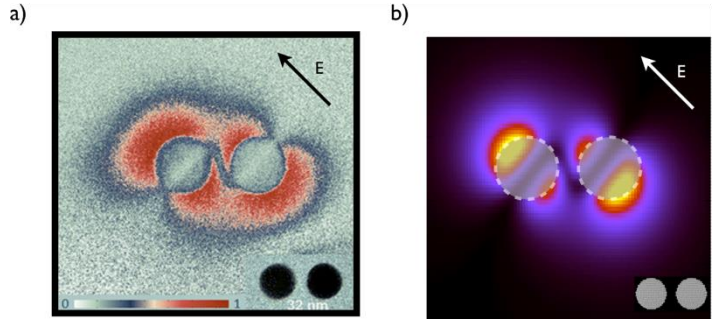


Figure 4.1-a) EELS map of two close-by silver nanoparticles
4.1-b Numerical simulation using the EELS GDM method.

Task 4.2: Imaging Calculations

Task 4.2.1 Imaging of interfaces

This task was not advanced due to a lack of sample availability. However, some key activities were merged with WP21.

Task 4.2.2 Modelling of Inelastic Scattering.

We have developed both multislice and Bloch wave computer codes, written originally in Matlab. Both methods solve the high-energy Schrodinger equation, which describes the electron-specimen interaction. In particular, a new Graphical user interface has been constructed and the codes now run on Windows and PC platforms, with a Macintosh version in Beta. All of these are freely available without charge and are disseminated through WP6.

Task 4.2.3 Comparison of Exit Wavefunction Reconstruction Methods.

Performance of three methods for exit wave reconstruction were tested as a function of radiation dose. The performance of these methods with decreasing dose was evaluated as a similarity index, or as a sum of squared deviations. The results show the recently developed MAL-based software performs noticeably better than the previously available methods at the lower doses, as indicated in Figure 4.2.

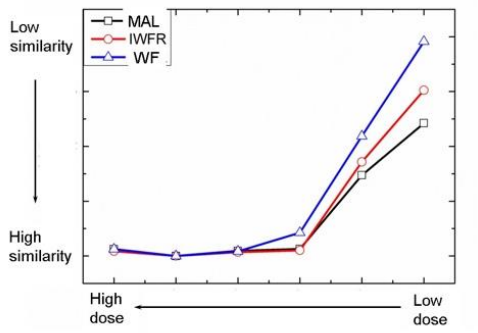


Figure 4.2. Similarity of the reconstructed exit wave using different algorithms (MAL, IWFR and WF) as a function of dose using the reconstruction at the highest dose as a reference. The highest similarity at the lowest dose is observed for the recently developed MAL-based algorithm.

Task 4.2.4 New 3D Wave Based Reconstruction Methods.

A method has been tested that quantitatively fits an atomic model to a reconstructed exit wave. For these calculations an exit wave for Si3N4 thin wedge sample was restored from a focal series of images using a newly developed MAL algorithm. The resulting model and the initial data are shown in the Figure 4.3.

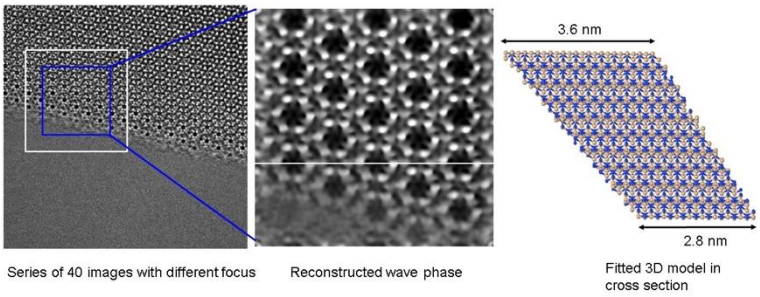


Figure 4.3. An image from a series of 40 images used to reconstruct the exit wave from the marked area of interest. Exit wave phase reconstructed from the focal series. 3D atomic model fitted to the reconstructed exit wave.

Significant results

This WP has produced numerous significant results. The list below highlights some of these related to each task.

- Task 4.1 EELS-GDM, a numerical framework for describing advanced spectroscopies
- Task 4.1 Development of EELS and application to GO and RGO
- Task 4.2 Quantitative comparisons of exit wavefunction reconstructions with variable dose
- Task 4.2 Improved image simulation software
- Task 4.2 A new method for 3D imaging using single image data

Work Package 6: Advanced Service provision

The purpose of WP6 is to provide users with advanced software tools and new methods developed within ESTEEM2. To this end we have collected 5 Digital Micrograph Scripts covering a range of topics together with 10 standalone software packages. This WP has also provided 25 protocols to assist TA users in optimizing their sample preparation and experimental methods. We have also completed a handbook describing experimental methods.

Task 6.1: Monitoring user satisfaction and determining future needs for service provision.

Service provision provided through TA within ESTEEM 2 is a critical component of the overall program. WP6 has monitored this aspect against initial targets set by the various partners. At the project end, 106% of the total TA access described in the original Description of Work has been provided. Moreover, during the project, we have regularly updated the provision of TA with respect to redistributions between instruments and partner laboratories to ensure that at any stage the service provision best matches the user access requirements.

To monitor the success of TA from a user perspective this WP has regularly monitored the reports provided by users following their visits. Two user meetings have been held during the project in which selected users were invited to present the results arising from their TA access and to make suggestions to the Governing Board as to how best to improve TA access.

Task 6.2: Harmonizing service provision.

Throughout the project as noted above we have monitored service provision as experienced by users to the ESTEEM2 TA scheme. Our aim is to ensure insofar as is possible that access to Research Infrastructure should be as uniform as possible across the centres providing TA. This is key as TEM transitions from laboratory based science to sustainable European infrastructure where this harmonization will provide the basis for any future EU model for TEM service provision.

We have also continually completed a series of "round Robin" Experiments in which identical standard samples have been carefully prepared and distributed among the labs offering TA. The results of experiments on these samples are now available and provide calibrations for each TA installation for users to access.

Task 6.3 Improving service provision

As already noted this Work Package has provided a range of standalone software modules and digital micrograph scripts and plugins that are accessible for all TA users. These are continually updated by the partners on a regular basis using a standard description that is published on the ESTEEM2 website. We have also published on the ESTEEM2 website a unique collection of protocols to assist TA users in optimizing their sample preparation and experimental methods and these have been well received by TA users. Over the lifetime of the project we have collected 15 software / scripts / plugins and 25 protocols.

Significant results

This WP has produced numerous significant results. The list below highlights some of these related to each task:

- Task 6.1 **User satisfaction**. The surveys have showed a huge satisfaction of the users regarding the ESTEEM2 TA scheme. More than 95% of the users consider that the ESTEEM2 process to access installations and the quality of support is adequate or excellent.
- Task 6.3 **DM Script**. **Oxygen Octahedra Picker**: a software tool to extract quantitative information from STEM (HAADF-ABF) images. It was written in Digital Micrograph (DM, Gatan Inc.) scripting language as a DM plugin. Centre-of-mass and 2D Gaussian fitting methods were implemented to locate positions of individual atom columns. It enables mapping of atomic column positions from HAADF and ABF images and quantification of both crystal lattice and oxygen octahedral distortions.
- Task 6.3 **Standalone Software**. **MulTEM:** A full GPU based multislice package for simulation of TEM and STEM images and diffraction patterns including the use of a novel scattering factor parameterisation based on a hydrogenic basis set. (https://github.com/Ivanlh20/MULTEM)

Work Package 7-19: Transnational Access

While the first ESTEEM project delivered 4224 access in five years (845 access-days per year), the original aim of ESTEEM2 was to provide 3450 access days to the user community in four years (862 access-days per year). In the end, 3669 access days (917 access-days per year) were granted, which is 6% more than initially expected. In total, 401 individual users have carried-out 359 TA projects.

One of the most important feature of advanced Electron Microscopy is that it is useful to a large variety of users, in different disciplines distributed across Europe. In the map below, it is clear that the provenance of TA users fits very well with a map of population distribution in Europe. Most TA access come from the Axis from London to Northern Italy, including Benelux, the Rhine valley, Bavaria, and Switzerland. European capitals are also well represented: Paris, Madrid, Dublin, Stockholm, Vienna, Berlin, Budapest, Athens, and Ankara have all provided several TA projects.

Figure 7-19.1: Map showing the geographic distribution of ESTEEM2 TA users. The map shows the city of provenance of TA users (in red) and the place where the experiment was carried out (in blue and yellow).

Considering the number of projects per country (figure 7-19.2), it appears that the UK, France, Germany and Spain have provided the majority of TA projects. They are followed by Italy, the Netherlands, and Switzerland. Moreover, ESTEEM2 has also managed to attract users from new member states including Slovenia, Hungary, the Czech Republic, Poland, Croatia, Slovakia, and Romania.

We observe more or less the same trend in ERC projects and thus conclude that ESTEEM2 managed to reach a balanced geographical coverage with respect to the current distribution of European funded research. Another similarity with ERC projects is that most users work in their country of birth. This is true almost everywhere except in the UK and Switzerland, which attract a lot of researchers from abroad. On the other hand, many Italian researchers work outside Italy.

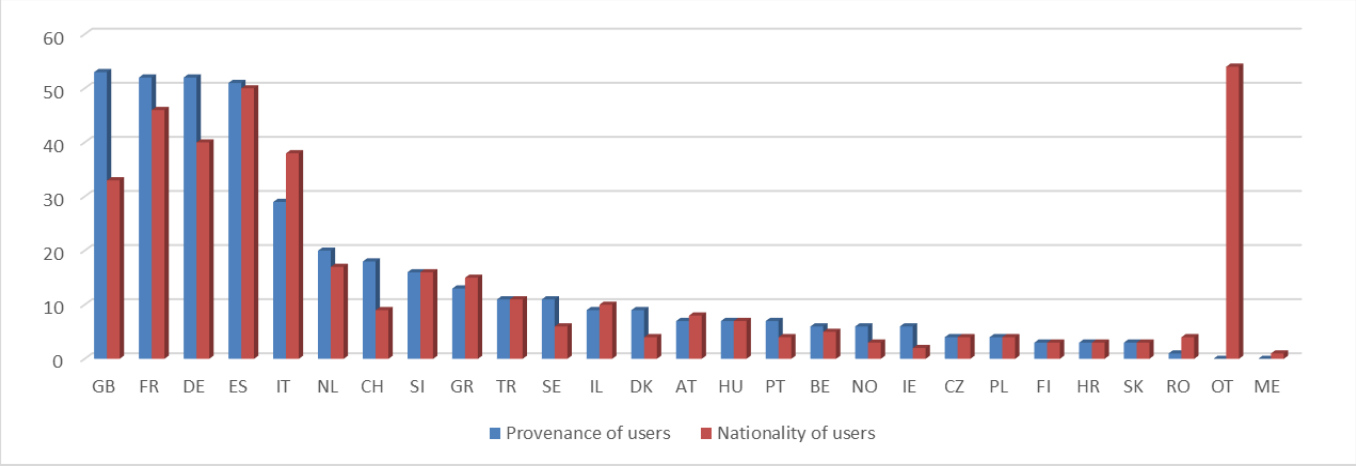


Figure 7-19.2: graph showing the provenance of users (in blue) and their country of origin (in red)

Another key feature of Electron Microscopy is that it is useful in solving important scientific problems in a large array of disciplines. For example, when invited to specify the main field of activity of their project, ESTEEM2 users named seven broad fields: Materials Science, Physics, Engineering and Technology, Chemistry, Life Science and Biotech, Earth Sciences and Environment, and Information and Communication Technologies (figure 7-19.3).

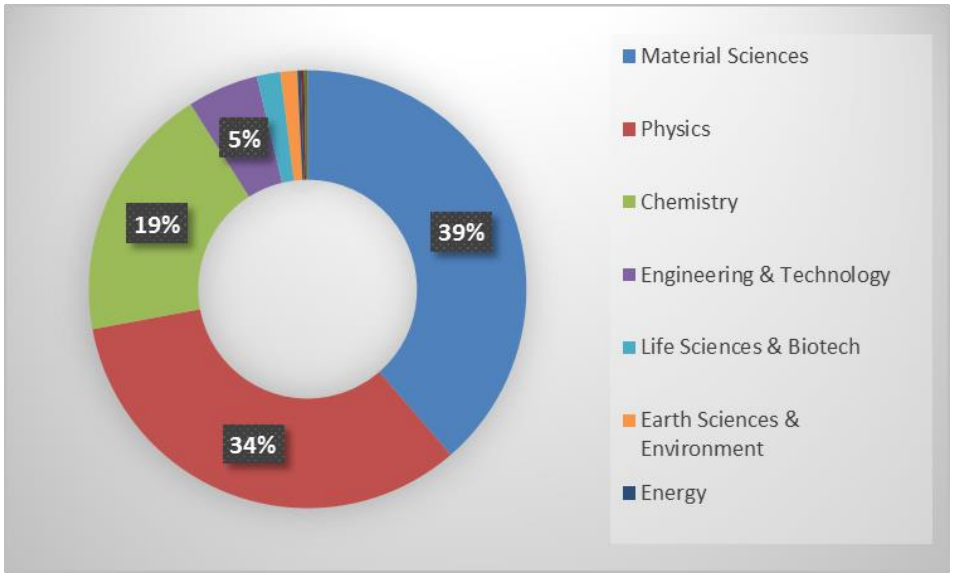


Figure 7-19.3: repartition of TA projects per scientific discipline

We now illustrate some examples of exemplar TA projects.

Materials Science – Knowledge based multifunctional materials

Polarity detection of translation boundaries in antiferroelectric $PbZrO_3$

TA project 20140311-Setter / Prof. Nava Setter, Université Polytechnique de Lausanne, Switzerland / Experiment carried out at ER-C Juelich

The discovery of conduction at domain walls in multiferroic $BiFeO_3$ has aroused widespread attention due to the potential device applications at smaller scale based on these multiferroic/ferroelectric oxides. In addition to domain-wall conduction, other peculiar properties are also found at domain walls, e.g. ferromagnetic antiphase boundaries in multiferroic hexagonal $Ba(Ti_{1-x}Mn_x)O_3$, and insulating domain walls with respect to domains in multiferroic $YMnO_3$.

In nonpolar materials, domain boundaries are also found to possess fascinating properties, which promises an alternative material basis towards future device applications. The Polarity of translation boundaries in antiferroelectric $PbZrO_3$ has been investigated in this project. It was shown that the previous experimentally reported polar property of the R_{III-1} type antiphase boundary can be well approximated by a strain-free rigid model. Based on this, the modelling investigation suggests that there are two additional polar boundaries, three antipolar-like boundaries and one antipolar antiphase boundary, cf. the figure blow. High-resolution STEM measurements reveal that the straight $\boldsymbol{R}_{III-1}$ type antiphase boundary can split into “sub-domains”. The Pb displacements reveal possible polarisation reversal inside the “sub-domains”, which suggests the occurrence of ferroic orders inside the translation boundaries.

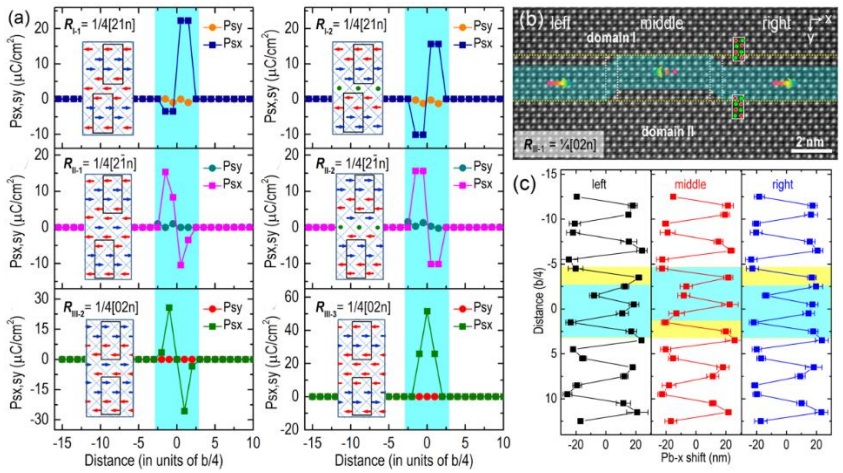


Figure 7-19.4: (a) Polarity of different type translation boundaries calculated based on the rigid models. (b) High-resolution HAADF-STEM image of PbZrO3 single crystal recorded along [001] direction. The RIII-1 type APB with "sub-domains" residing inside boundary is outlined. (c) The average Pb displacements for the left, middle and right part of the image along the boundary direction.

Materials Science – Other

Piezoelectric response of thin films

TA project 20140528-Noheda / Prof. Beatriz Noheda, Zernike Institute for Advanced Materials University of Groningen (The Netherlands) / Project carried-out at CNRS-CEMES Toulouse

Tetragonal Pb(Zr0.2,Ti0.8)O3 thin films relax by forming a c/a/c/a polydomain structure where c-domains (with vertical polarisation) alternate with needle shaped a-domains (or 90° domains with in-plane polarisation). The residual deformations of Pb(Zr0.2,Ti0.8)O3 thin film grown on SrTiO3 substrate were characterised using strain measurement techniques. Dark-field electron holography was carried out using the I2TEM-Toulouse microscope. Fig. 7-19.5(a) is an example of dark-field electron hologram showing a particular configuration of a-domains with opposite inclination. Fig. 7-19.5 (b) is the rotation field reconstructed from the hologram, which shows clockwise and anticlockwise rotation gradients on each side of the structure. As shown schematically in Fig. 7-19.5 (c), the rotations come from the constraints necessary to flatten the film onto the substrate.

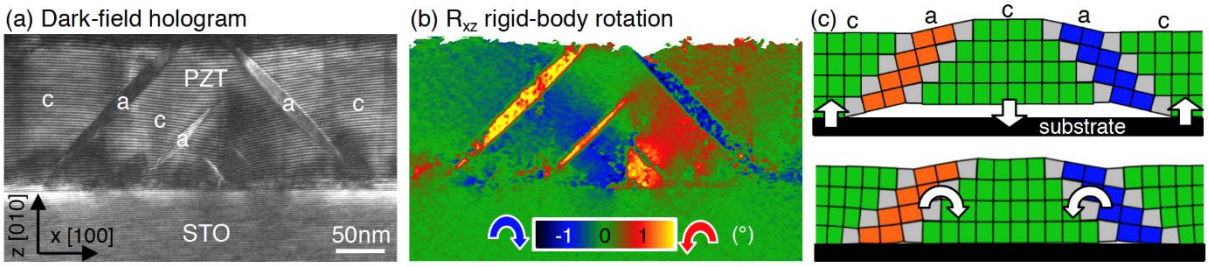


Figure 7-19.5: (a) (020) dark-field electron hologram of the PZT thin film in a region containing domains with opposite inclination. (b) Rigid-body rotation map Rxz (anticlockwise positive). (c) Representation of the lattice structure.

The dynamic behaviour of the domains was then investigated by in-situ TEM. A Hysitron was used to perform indentation and biasing experiments inside the microscope. Fig. 7-19.5 shows an example of indentation performed on a partial a-domain. Most of the a-domains extend from the interface to the surface of the film but some of them remain small, located near the interface. Those partial domains are unstable and can be extended by a mechanical pressure. Fig. 7-19.6 (a) is a TEM image showing a partial a-domain before indentation. During indentation (Fig. 7-19.6 (b)), the domain grows until it reaches the surface. After experiment, the domain comes back to the initial state.

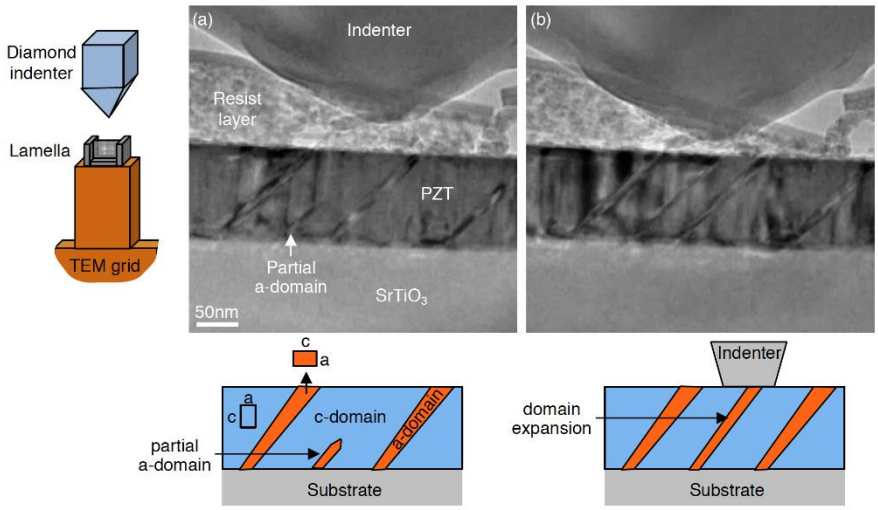


Figure 7-19.6: TEM image of the PZT thin film (a) before and (b) after indentation. The compression of the film induces the expansion of a partial a-domain.

Microstructural characterization of layered oxide materials used as positive electrode for Li-ion batteries

TA project 20160115-Reynaud / Dr. Reynaud CIC Energigune, Alava, Spain / Project carried-out at EMAT Antwerp

In the search for better battery materials several layered oxide structures such as Li_2MnO_3 and $Li[Ni_xMn_yCo_z]O_2$ have been investigated and their microstructure determined. Particularly the presence of superstructures and the super-structural ordering in the transition metal (TM) layers has been determined by a combination of electron diffraction and HAADF-STEM in a Cs corrected instrument. Apparently, a large number of stacking faults tend to appear in some of these materials while others showed large areas free of defects (see figure). We were also able to confirm the presence of TM cations in the Li layers both at the surface of the particles as well as at the bulk part. Finally, by the use of energy dispersive X-ray spectroscopy (EDS) we were able to successfully determine the chemical composition of the particles.

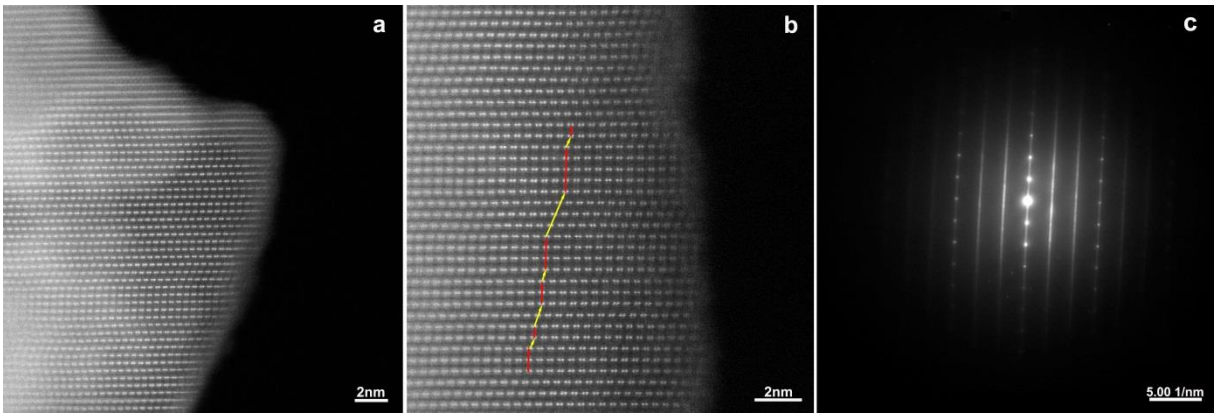


Figure 7-19.7: HAADF-STEM showed that a large number of stacking faults tend to appear in materials such as Li_2MnO_3

Nanoscale structural and chemical imaging of altered nuclear glass interfaces

(TA project 20130402-Hellmann) / Dr. Roland Hellmann, IS Terre, Grenoble, France / Project carried-out at TU Delft

Silicate glasses are durable solids, and yet they are chemically unstable in contact with aqueous fluids—this has important implications for numerous industrial applications related to the corrosion resistance of glasses, or the biogeochemical weathering of volcanic glasses in seawater. The aqueous dissolution of synthetic and natural glasses results in the formation of a hydrated, cation-depleted near surface alteration zone and, depending on alteration

conditions, secondary crystalline phases on the surface. The long-standing accepted model of glass corrosion is based on diffusion-coupled hydration and selective cation release, producing a surface-altered zone. However, using a combination of advanced atomic-resolution analytical techniques, our data for the first time reveal that the structural and chemical interface between the pristine glass and altered zone is always extremely sharp, with gradients in the nanometre to sub-nanometre range. These findings support a new corrosion mechanism, interfacial dissolution–reprecipitation. Moreover, they also highlight the importance of using analytical methods with very high spatial and mass resolution for deciphering the nanometre-scale processes controlling corrosion. Our findings provide evidence that interfacial dissolution–reprecipitation may be a universal reaction mechanism that controls both silicate glass corrosion and mineral weathering.

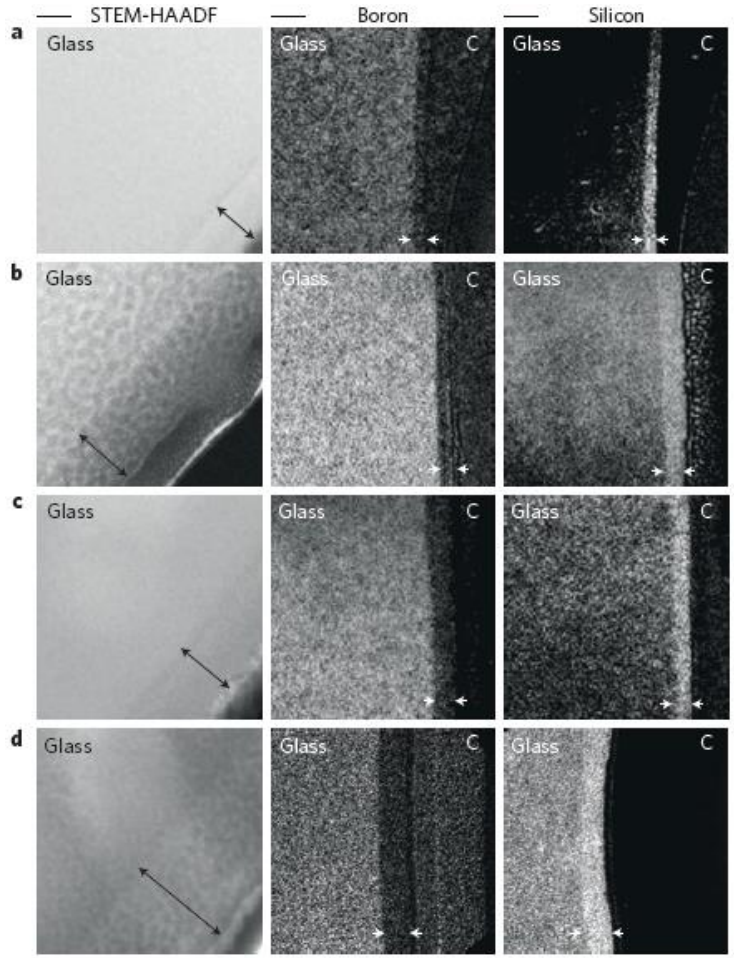


*Figure 7-19.8: STEM-HAADF images and EFTEM elemental maps of B and Si showing surface alteration in cross-section as a function of time. **a**, Four days. **b**, One month. **c**, Three months. **d**, Seven months. In each image the surface-altered zone is delimited by arrows; C denotes carbon—either a post-corrosion coating or a carbon-rich epoxy glue. The scale bars for the STEM images re 25 nm, for the EFTEM maps 100 nm. In the EFTEM maps, the grey scale intensity is proportional to the elemental concentration (that is, white, high concentration; black, low concentration).*

Physics – Condensed Matter Physics

MBE-grown GaAs Nanowires

TA project 20140218-Roddaro / Dr. Stefano Roddaro / Conziglio Nazionale delle Ricerche / Project carried out at University of Cambridge

A batch of specimens were received: a forest of GaAs nanowires grown by MBE, Device A27_TR with Ni/Ge/Au/Ni/Au contacts annealed for 3'30'' at 360°C, and Device A26_TR with Au contacts annealed for 2 hours at 320°C. Characterisation of the GaAs nanowires was performed using the JEOL 4000EX high resolution TEM (400 kV acceleration voltage). NWs have diameters of the order of 100 nm. GaAs nanowires have lengths of several microns, but small rod-like crystals are also present in the as grown material. Side surfaces are clean. Zincblende

and wurtzite domains were identified within the nanowires, with stacking faults running perpendicular to the wire axis. Single crystal zincblende NWs were also observed. In the SEM the nanowires appear faceted and crystalline.

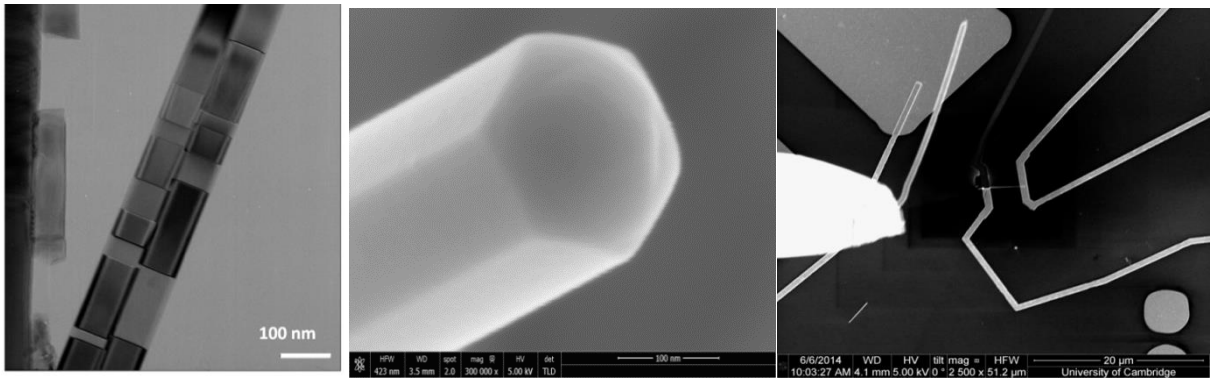


Figure 7-19.9 TEM and SEM – based investigation of MBE-grown GaAs nanowires

For Devices A26 and A27, several attempts were made to lift individual nanowires off the substrate using the Focused Ion Beam microscope, with the aim of depositing the nanowires onto TEM supports to investigate metal diffusion into the nanowire. Lifting and mounting individual nanowires without damaging the metal diffusion front was a very challenging experiment. Unfortunately, all attempts were unsuccessful due to charging of insulating substrate, contamination of the area under the beam and drift of nanowires/ion beam in the Helios SEM/FIB. Contamination is likely to be due to resist residues. No viable TEM specimen could be extracted from the devices, and this was reported to Stefano Roddaro's team.

In situ TEM study on the effect of mechanical strain on the resistivity of III-V semiconductor nanowires

TA project 20140331- Krogstrup / Prof. Peter Krogstrup, University of Copenhagen, Denmark / Project carried-out at Chalmers TH

Strain-engineering offers attractive possibilities for understanding and tuning the properties of semiconductors. If the band structure is changed due to strain, many material properties will be altered, including bandgap, effective mass, carrier mobility and dopant diffusivity. Recently, strain-dependent properties of semiconductor nanostructures have attracted research interest because these materials may be used as building blocks in next generation electronic devices. Semiconductor nanowires (NWs), in particular, are also found to be more flexible than their bulk counterparts because of their large surface-volume ratio. Thus, strain-engineering may play a significant role in tuning the material properties of these nanostructures and will lead to the discovery of some novel properties of these materials.

In this work, we have studied the electric transport property of individual InAs NWs under externally applied mechanical strain in transmission electron microscope (TEM) using an in situ TEM holder. The NWs were grown on Si substrates by molecular beam epitaxy and catalysed by Au nanoparticles. The diameter of the NWs is around 50 nm and the length of them is around 10 µm.

In situ TEM studies show that the resistance of the InAs NW increases gradually when the NW is bent while the I-V curves remain linear at different strain levels. As the strain is released, the NWs recover their original shape and the I-V curves coincide with the ones obtained without any force applied on the NW in the initial state. The mechanism of this phenomenon can be related to the modification of the band structure of the InAs NWs due to a change in lattice structure resulting from the mechanical strain.

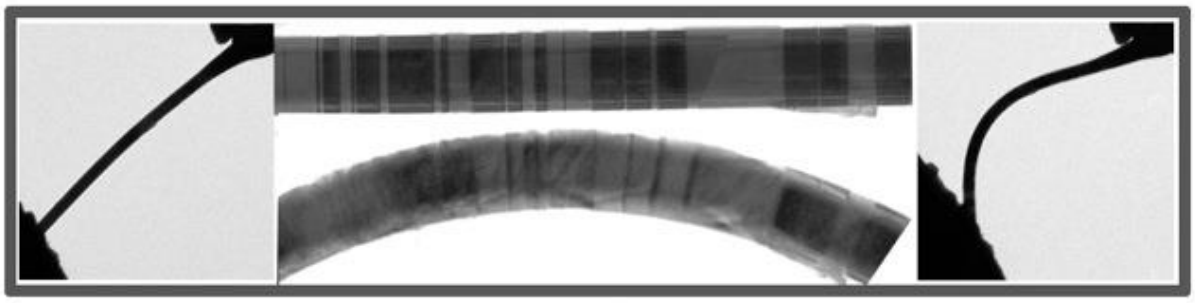


Figure 7-19.10: Bright field TEM images of an InAs nanowire bent in situ (far left, middle bottom and far right). The electrical transport properties are measured while the nanowire is bent. The diameter of the nanowire is about 50 nm. Stacking faults are seen in the TEM images in the middle.

Physics – Atomic & Molecular Physics

Morphological investigations of organic solar cells

TA projects 20140313-Moench and 20140615-Moench / Dr. Thomas Mönch; IAPP - Technical University Dresden, Germany / Project carried-out at AGH Krakow

Tobias Moench, MSc. visited IC-EM Platform in Krakow twice in 2014 and conducted the 60kV STEM-EDX research on meso- and nanoscale structure of the highly efficient small molecule solar cells.

During the stay of Mr Moench, the investigation of the C60 blended, oligothiophene derivatives (DCV5T-Me) - based absorber layer of the bulk-heterojunction (BHJ) organic solar cells were performed. Due to high sensitivity of the sample to irradiation damage, STEM-HAADF and STEM-EDX investigations were performed at 60 kV accelerating voltage. Absorber layer of the solar cell consisted of the blend of two or more organic materials. Various absorber morphologies were induced by different temperatures of substrates. STEM-EDX measurements allows to investigate all created morphologies, which were input to the further simulations. The relationship between processing, morphology, and efficiency of the final devices were established.

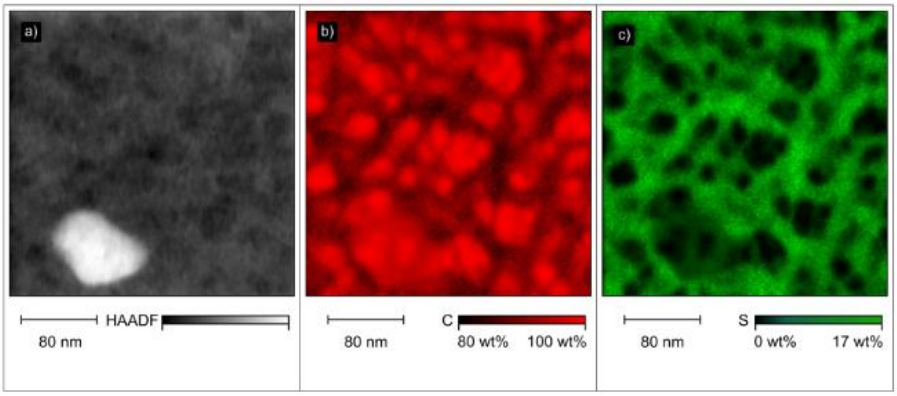


Figure7-19.11: STEM images of DCV5T-Me:C60 deposited at Tsub = 80 °C. The STEM-HAADF image a). The STEM-EDX images depicted in b) and c) show small C60-rich domains in a well-connected DCV5T-Me enriched network

The results of performed research are presented in the following paper:

T. Monch, P. Friederich, F. Holzmueller, B. Rutkowski, J. Benduhn, T. Strunk, Ch. Koerner, K. Vandewal, A. Czyrska-Filemonowicz, W. Wenzel, K. Leo: *Influence of meso- and nanoscale structure on the properties of highly efficient small molecule solar cells*, Advanced Energy Materials6(2016)1-10; DOI 10.1002/aenm.201501280

Engineering and Technology – Nanotechnology and Nanoscience

Atomic resolution STEM and EELS Analyses in CeO_2 and Cu_2O nanoparticles on GaN Nanowires surface

TA project 20130628-Eickhoff / *Prof. Martin Eickhoff, Justus-Liebig-Universität Giessen, Germany / Project carried-out at LMA-INA Zaragoza*

The objective of the project was the analysis of CeO_2, TiO_2 and Cu_2O nanoparticles grown at the surface of GaN and InGaN nanowires with the aim of improving its functional properties in catalysis, sensing or photonics. For this purpose, STEM imaging, and EELS and EDX spectroscopies were carried out in the Titan LB in UNIZAR in order to determine the following properties:

- Study of epitaxy and relative orientation between nanowire and oxide nanoparticles.
- Imaging the oxygen and nitrogen lattices at the interface by Annular Bright Field STEM.
- Elemental quantification of the oxide nanoparticles placed on the (In)GaN surface by EELS, as illustrated in Fig.17.1.
- Determination of the nanoparticles' oxidation state at sub-nanometre scale by EELS.

This work has made possible the correlation of this local analytical information with gas sensing photoluminescence experiments and a high impact publication is in preparation.

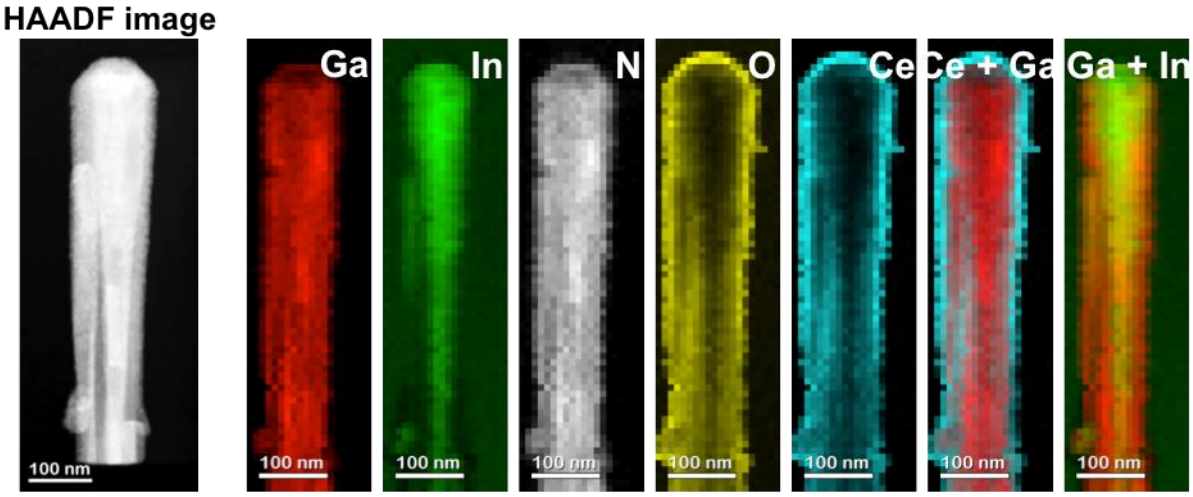


Figure 7-19.12.

STEM-EELS spectrum image of a group of InGaN nanowires coated with CeO2 nanoparticles merging together into a single NW. The reference HAADF image is shown with the elemental maps of the different chemical elements.

Isotope-enriched CVD Graphene

TA project 20140507-Nicolosi / Prof. Valeria Nicolosi, Trinity College Dublin, Ireland / Project carried-out at Oxford University

Isotopes are known to experience the kinetic isotope effect that causes different bond strengths in compounds formed of different isotopes. Using 80kV aberration corrected TEM at the University of Oxford, we make experimental observation of this effect in isotope-enriched Chemical Vapour Deposition grown graphene emerging from a remarkable increase in the $^{13}C^{13}C$ bond length and abundant existence of metastable edge features less commonly found in normal graphene.

The bond length was measured from a large uniform region of the isotope graphene to be 0.166 nm ± 7.34 pm (measurement standard error plus a pixel size). This is considerably longer than that of normal graphene (0.142 nm), indicating the altered bonding characteristic of isotope graphene. Such findings of an elongated isotope bond length match literature findings using SSNMR.

Uncommon edges features such as extended regions of disorder and extend Klein Edge Doublets (KLD) are recorded as described in the figures below. They are interesting for the potential to change local electronic structure and act as potential dopant site receptors because they are stable enough to exist for easy TEM image acquisition before any further change or sputtering of C atoms.

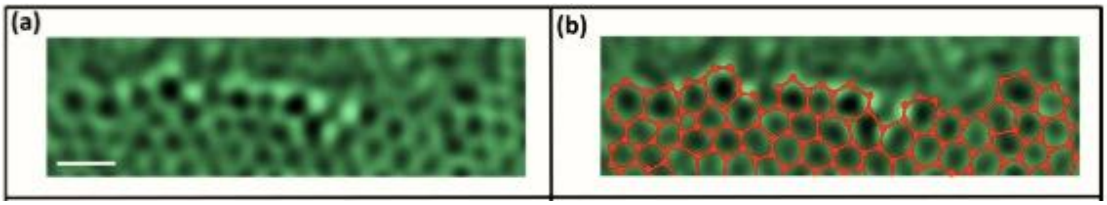


Figure 7-19.13 Highly disordered edges forming distortions further into the crystal. Scale bar is 0.5 nm

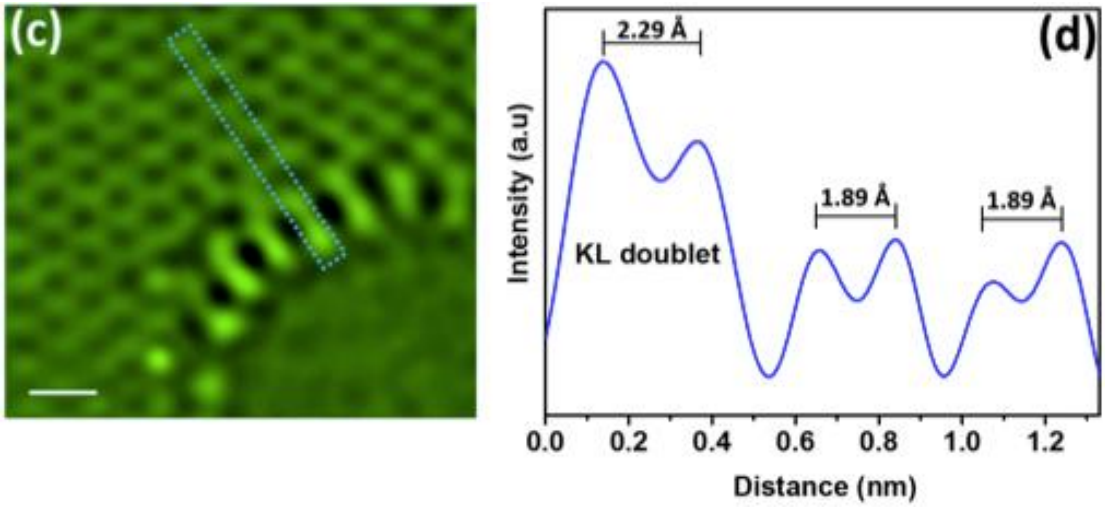


Figure 7-19.14: Extended array of dangling carbon dimers. Solitary or paired sets of dangling carbon dimers have been observed in traditional CVD graphene, but such an extended array of these dimers called Klein Edge Doublets (KLD) is an interesting and new structure unique to this isotope graphene. Scale bar is 0.5 nm.

Chemistry

The Role of Boron in the Structural Formation of Long Persistence Eu2+ and Dy3+ co-doped Sr4Al14O25

TA project 20140201-OwYang / Dr. Cleva Ow-Yang, Sabanci University, Istanbul, Turkey / Project carried-out at CNRS-LPS Orsay

The objective of this request was to elucidate the role of Boron as a dopant in the structural formation of long persistence $(SrO)_4(Al_2O_3)_7$ doped with Eu^{2+}, Dy^{3+}. Boron is known to extend dramatically the afterglow persistence, which was serendipitously discovered when it was used as flux agent. Preparation of the stoichiometric $Sr_4Al_{14}O_{25}$ compound doped with 1 mol% Eu^{2+} and 1 mol% Dy^{3+} by sol-gel processing (a modified Pechini method) produces a mixture of phases as revealed by x-ray diffraction analysis: $Sr_4Al_{14}O_{25}$, $SrAl_{12}O_{19}$, $SrAl_4O_7$, and other non-equilibrium phases. However, the presence of boron (*i.e.*, 0.5, 2, and 4.5 mol % B) results in a predominantly $Sr_4Al_{14}O_{25}$ phase with a limited presence of $SrAl_{12}O_{19}$. The effect of B incorporation on the crystallization kinetics was investigated

previously by thermal analysis, x-ray diffraction analysis, and on microstructural evolution by TEM imaging and diffraction analyses. The nanoscale cathodoluminescence performed through this TA made it possible to investigate, as a function of Boron doping, the valence state as well as the crystallographic site of the Eu in the matrix. The results are submitted for publication, and this TA worked well enough to trigger a stronger collaboration (FET-OPEN submitted between the platform and the applicant)..

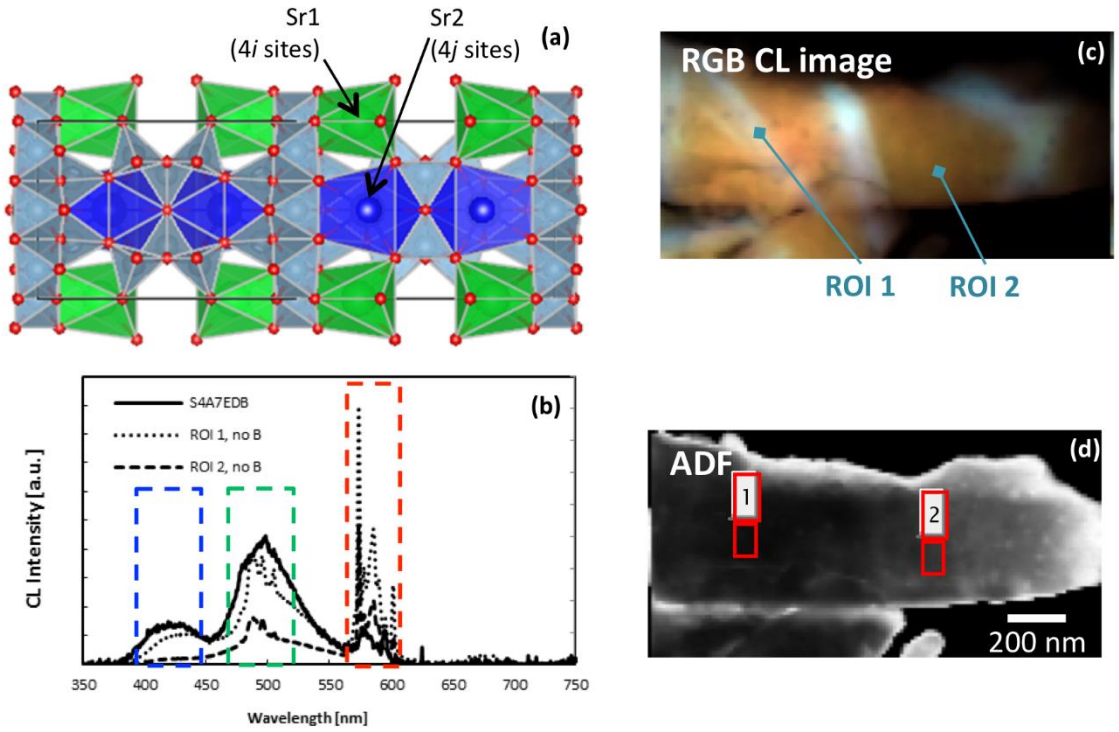


Figure 7-19.15: (a) the crystal structure of $Sr_4Al_{14}O_{25}$: green = Sr^{2+} in 4i Wyckoff sites (Sr1), blue = Sr^{2+} in 4j Wyckoff sites (Sr2), gray = Al^{3+}, red = O^{2-}; (b) cathodoluminescence (CL) emission spectra from both boron-doped and boron-free S_4A_7EDB specimen (from 2 different regions analyzed); at ca. 420 nm, emission from Eu^{2+} in the Sr2 sites (i.e., the Sr^{2+} sites in blue); at ca. 490 nm, emission: from Eu^{2+} in the Sr1 sites (i.e. the Sr^{2+} sites in green)[26]; Region 1 a plate-like grain; Region 2 equiaxed SA particles; (c) RGB image formed from CL emission from the spectral regions indicated: blue from 402-456 nm, green from 476-525 nm and red from 566-607 nm; (d) corresponding annular dark field image of the entire region analysed by CL spectrum imaging.

Earth Sciences and environment

Study of black carbon particles with HR-STEM and HR-EELS

TA projects 20141212-Hagemann and 20150703-Hagemann / Dr. Nikolas Hagemann, University of Tübingen, Germany / Project carried-out at FELMI-ZFE Graz

Biochars (black carbon particles) change their structure and properties in a complex manner as they interact with plant roots, soil micro-organisms, soil dissolved and solid organic mineral matter. A new specimen preparation method based on the special requirements (ultrathin large original non-contaminated areas from the functionalized area on the surface of the black carbon particles) had to be developed. STEM-HAADF images and EELS near-edge fine structure (ELNES) at high energy resolution were used to provide information on the local structure and bonding of specific types of atoms at the surface of fresh prepared, composted and aged biochar types (Figure 7-19.16). X-ray mapping in the STEM was additionally used to identify different mineral nanoparticles.

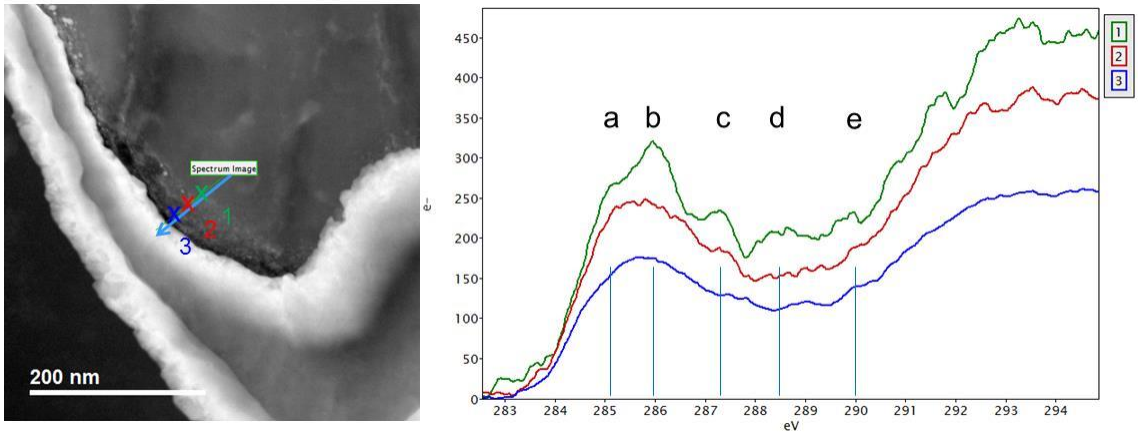


Figure 7-19.16 N-K

ELNES spectra from two regions in the KonTiki composted biochar sample. The functional groups are indicated with a: 398.8 eV –> pyridinic; b: 400.0 eV –> imine; c: 401.5 eV –> amide / peptide; d: 403.7 eV –> nitro.

Life Science and Biotech

Interplay of organic matrix and amorphous calcium phosphate strengthens the isopod claw

TA project 20160229-Vittori / Dr. Milos Vittori, University of Ljubljana / Project carried out at MPG-StEM Stuttgart

Animal skeletons are high-performing composite materials that may help inspire materials and designs in a broad spectrum of industrial and biomedical applications. The study of various skeletal elements can provide important insights into evolutionary solutions to mechanical demands of animal locomotion, feeding and reproduction, as well as the mechanisms controlling skeletal formation and biomineralization.

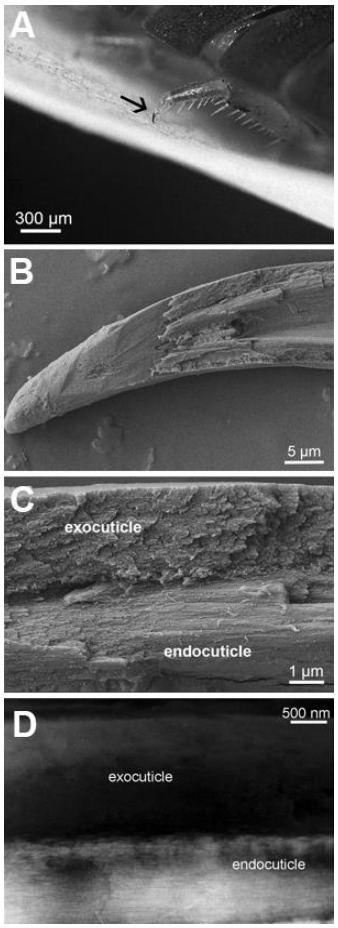
The extracellular matrix forming the crustacean exoskeleton comprises chitin-protein fibres embedded in a calcified inorganic matrix that consists of calcite and amorphous calcium carbonate. In crustaceans, the cuticle can be subdivided into a thin external layer - the epicuticle – and two internal layers, which are heavily calcified – the exocuticle and the endocuticle. The crustacean cuticle generally consists of stacked sheets of parallel chitin-protein fibres, which helicoidally shift their orientation in each sequential sheet, resulting in a structure referred to as the Bouligand pattern. This organization of the fibres strengthens the cuticle in different directions, enabling the exoskeleton to withstand unpredictable loads.

In our study, we analysed the structure and composition of the walking leg claw of the woodlouse *Porcellio scaber*. Woodlice are terrestrial crustaceans that support their bodies with 7 pairs of legs, each ending in a claw. The claws are thin skeletal elements predominantly subjected to unidirectional loads. To study the nano-structure of the matrix, we imaged fractured claws with field-emission scanning electron microscopy using a JEOL 7500F microscope. We then analysed the elemental composition and the distribution of mineral components in the claws with energy-dispersive X-ray spectroscopy (EDX) and electron energy-loss spectroscopy (EELS) combined with scanning transmission electron microscopy (STEM) imaging at high spatial and high energy resolution using Zeiss SESAM and JEOL ARM200F microscopes at different accelerating voltages.

Our results demonstrate that the external exocuticle of the claw is not calcified and is heavily brominated instead. The endocuticle, on the other hand, is mineralized predominantly with stable amorphous calcium phosphate, which is a highly unusual feature of an animal exoskeleton. Furthermore, we established that the claw endocuticle is highly structurally anisotropic, consisting of axially oriented chitin-protein fibres and amorphous calcium phosphate particles, all oriented in the direction of loading.

The presence of amorphous calcium phosphate at the mineralized endocuticle of the non-calcified, brominated external exocuticle may help increase fracture resistance of the claw cuticle. The brominated exocuticle, which is likely more elastic than the mineralized endocuticle, is distributed in areas subjected to maximum stress during axial loading of the claw. These structural and compositional features of the claw cuticle likely result in greater resistance to fracture and wear when exposed to axial loading.

This work has been published in *Vittori, M.; Srot, V.; Zagar, K.; Bussmann, B.; van Aken, P.A.; Ceh, M.; Štrus, J.:* Journal of Structural Biology **195** (2016) 227–237.



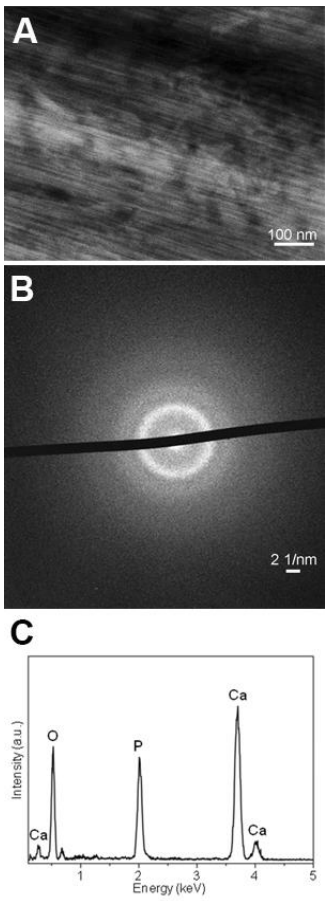


Fig. 7.19.17 A: *The claw of* Porcellio scaber. ***B:*** *SEM image of the fractured claw.* ***C:*** *Higher magnification SEM image of the claw, showing the exocuticle and the endocuticle with unidirectionally oriented fibres* ***D:*** *HAADF-STEM image of the region in* ***C****, showing the greater electron density of the claw endocuticle.*

Fig. 7-19.18. A: *HAADF-STEM image of the claw endocuticle, showing unidirectionally oriented particles of calcium phosphate.* ***B:*** *Electron diffraction of the area region in* ***A****, demonstrating the amorphous nature of the calcium phosphate.* ***C:*** *EDX spectrum of the region in* ***A****, characteristic of calcium phosphate.*

Work Package 20: Electron Diffraction

Electron diffraction and associated electron crystallography, to study atomic structure and microstructure (orientation, strain) in 2D and 3D, has undergone a renaissance in recent years. Modern instruments, with dedicated 3rd party equipment, are capable of recording many thousands of diffraction patterns over a region of interest in just a few minutes creating a 4D data set for further analysis. Such a rich data set contains a wealth of information and efforts have focussed on how best to reduce such 'big data' to manageable and interpretable components using e.g. machine learning algorithms. Modern computation enables highly detailed dynamical simulations that can run with many models so as to find a best fit to any diffraction pattern. New algorithms are being developed to aid the refinement of atomic positions for an unknown crystal structure or the determination of charge bonding density. In addition, by creating very large supercells it is possible to simulate the thermal vibration of atoms and molecules and to refine that against experimental data, often in the form of diffuse scattering.

Task 20.1: Structure Determination from Electron Diffraction

Within this task there were three key areas of research: (i) providing a starting model from precession electron diffraction (PED), (ii) providing a starting model from STEM, (iii) structure determination and refinement, leading on to Task 2. In the first area, as an example, nanoscale organic crystals of a pharmaceutical compound embedded within an amorphous matrix was studied with PED such that each crystal provides a single 'random' diffraction pattern before beam damage causes amorphisation. The unit cell of the unknown crystalline phase was determined and the polymorph of the pharmaceutical was identified. Combining tomographic acquisition with PED enables the reconstruction of the 3D reciprocal lattice and measure associated intensity data post-facto. The structure of amorphous and nano-crystalline materials was determined using a pair distribution function approach; the technique was applied to a variety of materials including intermetallic alloys, opals and amorphous silica. The remarkable sensitivity of new electron detectors has enabled diffraction patterns to be acquired from the most beam-sensitive of organic compounds. By combining fast low-dose electron diffraction tomography (tilt series of diffraction patterns) with novel detector technology it has been possible to determine the structure ab initio of two organic compounds, namely carbamazepine and nicotinic acid. In the second area, atomic resolution images with chemical sensitivity given by atomic resolution EDX were used as a real space solution to determine a structural model. In the case of Ni-base superalloys, we saw a remarkable superstructured ordering of Ni in the γ'' phase. STEM HAADF images were also investigated to see if by quantifying the grey scales they could be used as input for structure solutions. In the third area, the optimum way to refine PED data was established. It is clear that under certain conditions (precession angle, thickness) and for certain crystal structures a good refinement is achievable but further work is required to extend this more generally.

Task 20.2: Refinement of the Crystal Potential

Structure determination using electron diffraction can yield atom positions almost as accurate as those from X-ray single crystal diffraction but using samples many orders of magnitude smaller. Once a good starting model is available, atom positions can be refined, with any remaining non-determined atoms found. We have developed a software package, ELSTRU, for full dynamical structure refinement. Moreover, bonding leads to non-spherical charge distribution, and electron diffraction is known to be sensitive to such bonding charge density. ELSTRU is now also able to do this via a multi-pole formalism. Such refinement requires starting values close to the truth and modern first principle quantum-mechanical ab-initio code, like VASP can be used to provide such starting values. Elastic scattering of electron vortex beams on magnetic materials leads to a weak magnetic contrast due to Zeeman interaction of orbital angular momentum of the beam with magnetic fields in the sample. The magnetic signal manifests itself as a redistribution of intensity in diffraction patterns due to a change of sign of the orbital angular momentum of the electron vortex beam. Quantitative CBED analysis often requires a comparison with numerical simulations and/or experimental references. A method was developed to provide the latter in parallel to the actual CBED experiment. Using a condenser biprism, the CBED pattern is split in two half-CBED disks, permitting the acquisition of two CBED patterns in one image. Dynamical scattering theory was applied also to dark-field holography to provide a more straight-forward interpretation of dark-field holograms of z-dependent strain fields (e.g. surface relaxation effects).

Task 20.3: 2D and 3D Orientation Mapping

Work in this area was undertaken across many different materials, both inorganic and organic, and a number of techniques were developed. For example, the orientation relationships in Ti/Al alloys were investigated, the texture of organic semiconducting structures was studied and Ni-base superalloys were used as a platform to show how scanning PED can provide orientation maps of quality equal to that of many SEM-based EBSD orientation maps (Euler maps) but with near-nm spatial resolution. This approach was extended to 3D, combining orientation

mapping with tomography to enable a form of 6D microscopy in which at every 3D real space pixel a full 3D orientation relationship is known with its neighbouring pixel. Extending this further still, by analysing the data correctly, it is possible to back out strain components at every reconstructed voxel, with a proof-of-principle application made to a semiconducting nanowire.

Task 20.4: Measurement of Lattice Vibration and Phonon Scattering

Electron diffraction has been shown to be a powerful tool for studying dynamics and disorder in a wide range of different materials systems, given the sensitivity to small changes in atomic positions for even light elements**.** We developed techniques focussed primarily on new generation organic semiconductor materials such as TIPS-pentacene and TMTES-pentacene, in order to understand the deleterious effects of lattice vibrations on the transport properties. Ultra-fast algorithms implemented on graphical processing units (GPUs) were developed ta the same time in order to simulate diffraction patterns accurately and efficiently.

Significant results

Many high quality papers have been published in JRA1 including papers in Nature journals, Acta Cryst, Physical Review, etc. We give a non-exhaustive selection of significant results:

- **Dynamic scattering formalism for dark field electron holography** which facilitates the projection of 3D strain fields by a simple weighting integral enabling the development of tomographic strain reconstruction techniques. [A. Lubk, et al. Ultramicroscopy, 2014, 136, 42 – 49].
- **Scanning precession electron tomography** was developed for three-dimensional nanoscale orientation imaging and crystallographic analysis. [A.S. Eggeman et al. Nature Communications doi:10.1038/ncomms8267]
- **Measurement of molecular motion in organic semiconductors by thermal diffuse electron scattering.** Molecular motions in an organic semiconductor were determined from dynamical refinement of experimental thermal diffuse electron diffraction measurements. [A.S. Eggeman et al. *Nature Materials* **12** (11) 1044-1048; S Illig et al. Nature Commun 2016, 7 10736]
- **Ultrafast electron diffraction pattern simulations using GPU technology** The principles for accelerated computation of dynamical scattering using graphical processing units are discussed with an example of diffuse scatting in silicon. [A.S. Eggeman, et al.*Ultramicroscopy* **134** 44-47]
- **The ELSTRU package.** A structural refinement package was made available including the possibility of charge bonding density determination.
- **Ab-initio structure determination of organic nanocrystals.** Using a new Timepix detector the structure of organic compounds were solved using electron diffraction at room temperature. [E. van Genderen et al, 2016, Acta Cryst A 72 236-242.]
- **Use of vortex beam electron diffraction to measure magnetic properties.** This utilises the Zeeman interaction of the orbital angular momentum of the beam with magnetic fields in the sample. **[**A. Edström et al. *Phys. Rev. Lett*., 2016, 116, 127203]
- **Successful use of random diffraction tomography** to identity the crystal structure of a pharmaceutical compound. [S. Nicolopolous et al. (2014) Proc IUCr Congress (Montreal)]
- **Atomic resolution STEM EDX** to provide a starting model for ordered phases in Ni-base superalloys [K. Kulawik, et al. (2015) Materials Characterisation, 100, 74-80]

Work Package 21: Imaging

The overarching aim of this activity was to develop infrastructure for quantitative atomic-resolution imaging in the electron microscope. The techniques included in the work package are those associated with conventional high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscope (STEM).

At the start of the ESTEEM2 project, quantitative interpretation of HRTEM and STEM images had been investigated for a number of years. The strong interaction between electrons and matter requires experimental data to be compared with detailed simulations. The work in this JRA has focused on both new modes for imaging and work to improve the match between simulation and experiment without the need for free fitting parameters. The aim of both of these is to improve the inversion of HRTEM and STEM data to experimental parameters.

Task 21.1: Imaging Mode Selection and Data Acquisition

This task is further divided into three subtasks. In each of these subtasks, there have been two principal aims: (i) to explore how the optimal imaging mode from those available can be matched to specific sample problems and (ii) to develop new imaging modes to extend the capability of TEM and to extend the range of capabilities of the technique.

The aims (i) above have been addressed though more than 50 publications across the range of partners in this JRA examining a wide range of materials which have then been compared at the annual WP partner meetings. Broadly the conclusions are as follows:

STEM ADF (Task 21.1.1):

The imaging mode is non-linear (is not sensitive to single electron scattering) and is inefficient with many of the scattered electrons not being detected. It is therefore more suited to high atomic number elements. It also suffers from issues from the scanning nature of the image formation such as scan distortions. Its incoherent nature makes quantitative interpretation simpler, for example through the use of cross sections. The low angle, medium angle and high angle variants of ADF imaging can balance interpretability against efficiency.

STEM ABF (Task 21.1.1)

The imaging mode is simple to implement and sensitive to light elements. Two mechanisms lead to contrast: channelling which is non-linear and relies on multiple scattering; and phase contrast if aberrations are present. The two contrast mechanisms present make this mode hard to interpret quantitatively.

STEM pixelated detectors (Task 21.1.1)

Through ptychography, data from pixelated detectors can provide linear imaging (single scattering detection) and is therefore a highly efficient imaging mode. Such detectors can also provide angular resolved dark-field data which make reveal enhanced information such as the presence of strain. It needs specialised hardware which is starting to emerge, and there are challenges with handling the large amount of data produce.

HRTEM / Exit-wave (Task 21.1.2)

It provides linear imaging, but the challenge of getting a fit to simulations without the use of fitting parameters remains. Other modes of using data from the conventional TEM mode, such as the measurements of probability currents, have been developed as part of this JRA

Atomic resolution spectroscopy (Task 21.1.3)

Spectroscopy can provide unambiguous chemical information at atomic resolution. Challenges addressed in this JRA include the calibration of detector collection angles, including the effects of channelling which complicates quantification, and overcoming the issue of the spectroscopic signals being weak compared to elastic scattering.

Task 2: Instrument Parameter Measurement and Control

Work in this task has been steered by the requirements identified through task 1. One focus of the work has been developing methods for precise detector calibration to enable data quantification. Achievements include the modelling of the collection angles for multiple EDX detectors, and a method of mapping STEM imaging detectors accurately. The problem of scan distortions and instabilities in STEM has been addressed through the development of an image acquisition method that involves the fast acquisition of multiple images followed by non-rigid image registration.

Task 3: Inversion to Obtain Physical Measurements

Within this task, methods to invert experimental data to measurements of physical sample parameters have been investigated. Two principal methods have been used: statistical parameter estimation theory, where the discrete nature of atoms is used as prior information to enable data quantification, and direct comparison to simulations. The latter has also been combined with prior information, such as the use of minimum energy constraints to allow 3D reconstruction.

Significant results;

This JRA has produced numerous significant results. The list below highlights results related to each task that have led to the creation of a new capability that can be offered to users to provide enhanced quantitative measurements.

- Task 21.1.1: The first use of ptychography with a fast pixelated detector in STEM to enable simultaneous phase imaging alongside incoherent modes and the application to the structure determination of a complex nanostructure. [Yang et al. Yang et al, Nat Commun, 7 (2016) 12532. DOI: 10.1038/ncomms12532]
- Task 21.1.2: The measurement of lateral probability currents of scattered electrons. [Lubk, A. et al. Phys. Rev. Lett. 115 (2015) 176101]
- Task 21.1.3: Quantitative EDX mapping. [Kothleitner et al. Phys. Rev. Lett. 112 (2014) 085501.]
- Task 21.2: Fast image acquisition followed by non-rigid registration. [Jones et al. Advanced Structural and Chemical Imaging. 1 (2015) 8.]
- Task 21.3: A method to calculate the scattering from mixed element columns. [van den Bos et al. Physical Review Letters 116 (2016) 246101]

Work Package 22: New types of electron spectroscopy.

The aim of this WP was to develop new, versatile techniques, methods and equipment for performing spectroscopy in the electron microscope. The motivation relied on several observations made on the situation of electron spectroscopy (essentially Electron Energy Loss Spectroscopy, EELS, and in a lesser extent, Cathodoluminescence, CL) at the end of ESTEEM1.

- Due to the development of aberration correctors, it became possible to image, at the atomic level, the chemistry (i. e. the type of atoms) in materials.
- New types of electron beams, namely vortex beams, were discovered and used to unveil magnetic properties in materials.
- It became possible to study the optical properties of nanoparticles and nanostructures with deep subwavelength resolution.

This WP goals were therefore to (i) study the valence and electronic structure of materials at the atomic scale mapping the so-called EELS fine structures, especially for functional magnetic or multiferroic materials, (ii) develop versatile vortex beams and using them for nanometre resolution magnetic state investigation, and (iii) develop new methods in EELS and CL mapping and applying them to functional optical materials. Beyond the success of these approaches, new and unforeseen avenues have been explored, all discussed subsequently.

Task 22.1: Magnetic information from EELS: approaching the atomic scale.

In this task, we aimed at shaping the electron beam so that it can be put in a state likely to enhance the magnetic information that can be retrieved after interactions with the sample. Numerous strategies have been developed to successfully produce vortex beams with high current and small sizes (now down to the atomic level) to understand the interaction of vortex beams with samples. In addition, paths towards *in situ* controllable phase plates for forming vortex beams have been successfully explored, including the report of an *in situ* switchable phase plates, or the use of aberrations control to specifically shape the beam. New forms of phase-shaped beams (beyond vortices) have been developed to match specific symmetries (see applications in Task 3). This work has been complemented by temperature-dependent Electron Magnetic Chiral Dichroism experiments, revealing a breaking of the local ferromagnetic order with temperature.

Task 22.2: New spectroscopy for local electronic structure mapping.

In this task, we aimed at optimizing the experimental set-ups to obtain the maximum amount of spectroscopic information concerning valence and bond directionality at atomic resolution. Several important physical effects, such as charge accumulation, charge ordering and magnetic dichroism have been unveiled at very high spatial resolution. All have been achieved on materials of technological interest for applications in spintronics or oxytronicsWe also advanced instrumentation and methodological developments. This included the use of processional EELS measurements to eliminate the effects of channelling in EELS. An important effort towards the use of compressive sensing in EELS spectral-imaging was made in relation to WP23: three dimensions mapping of oxidation states with nanometer scale. Finally, quantitative EELS/EDX mapping has been performed for the first time at atomic resolution.

Task 22.3: New types of electron based nano-optical spectroscopy techniques

In this task, we aimed at exploring and enhancing the capabilities of existing high energy resolution electron spectroscopy (monochromated EELS, Cathodoluminescence) to explore optical properties of nanomaterials at the nanometre scale. First, several original plasmonic structures with important applications for electromagnetic confinement have been explored experimentally and/or theoretically. Second, methodological and instrumentation developments, supported by a large theoretical effort, have been pursued. This led to the first experimental comparison of EELS and CL plasmonic signatures, the use of phase-shaped probes for plasmonics, several demonstrations of plasmon tomography and deeper insight in plasmon holography. Moreover, quantum intensity interferometry for cathodoluminescence that used single photon emitters' characterization has been developed. .

Finally, a large effort in developing and improving analysis tools such as Hyperspy and EELSMODEL has been performed in parallel with the above tasks.

Significant results;

Many high impact papers have been published in this JRA including 1 Nature, 1 Nature Material, 1 Nature Communication, 1 Nature Physics, 10 Phys. Rev. Lett, several Nano Letters, etc…We give hereafter a non-exhaustive selection of significant results, all being "first" in their respective domains:

- **Realisation of a single vortex mode of high current** making use of a magnetic nanoscale needle. This result is significant both on the experimental side to produce vortex beams as well as on the theoretical side as it represents an approximation to a magnetic monopole. [A. Béché, et al., Nat. Phys. (2014)]
- **Direct experimental evidence of Fe^{2+}-Fe^{3+} charge ordering** at room temperature in hematite-ilmenite epitaxial thin films has been demonstrated with a strong modulation of the Fe^{2+} valence state along the c axis. This will help understanding further the origin of its geomagnetic properties [Bocher et al., PRL, (2013)].
- **Mapping of oxygen coordination in complex oxides**. The fine structure of transition metal excitation edges was shown to provide detailed information on the coordination that can be used to map coordination differences on a local, atomic scale [S. Turner, et al., *Appl. Phys. Lett.* (2012)
- **An experimental comparison between atomically resolved EELS and EDX chemical mapping**, together with comparison with simulations, has allowed to get *absolute scale quantitative* comparisons between experiment and quantum mechanical calculations for both techniques [Kothleitner et al., PRL, (2014)]
- **Measurement of the charge redistribution in two-dimensionally strontium (Sr)-doped La2CuO4 superlattices**, in which single LaO planes are periodically replaced by SrO planes [Wang et al., ACS App. Mat. and interf., 2016].
- **Three dimensional reconstruction of a plasmonic response** at sub-10 nm has been performed thanks to a combination of tomographic techniques and advanced data analysis [Nicoletti et al., Nature, (2013); Collins et al., ACS Photonics (2016].
- **Quantum nanoptics experiments** have been performed by measuring single photon emission in nano-diamond [Tizei et al., PRL 110, 153604 (2013)] and hBN [Bourrellier et al., Nano Letters (2016)]
- **Determination of the fundamental scaling laws ruling plasmon properties** in flat plasmonic structures [Schmidt et al., Nature Comm. (2014)].
- **Use of phase-shaped beams with dipolar behaviour to measure the full symmetry of plasmons** at the nanometre scale. This method shows some resemblance to the widespread use of polarised light for the selective excitation of plasmon modes but adds the advantage of locally probing the response of individual plasmonic objects and, in principle, a far wider range of symmetry selection criteria [Guzzinatti et al., Arxiv. (2016)].

Work Package 23: 3D nanometrology

At the start of the ESTEEM2 project, electron tomography was considered as a technique to investigate the 3D structure of (nano)materials with a resolution at the nanometre level. The focus was on the investigation of the morphology of the materials and most of the results were only interpreted in a qualitative manner. The objective of this JRA was to obtain precise and quantitative measurements of the 3D structure but also of properties in 3D, in some cases at the atomic scale. Since the start of the project, great progress was made based on developments that include the design of new tomography holders, acquisition schemes and reconstruction algorithms. In this manner, the 3D characterisation of nanomaterials was taken to a completely new level.

Task 23.1: Reconstruction Algorithms and Quantification

Misalignment of tomographic tilt series hampers a reliable quantification of 3D reconstructions. Therefore, different procedures were proposed that provide both a correction of displacements with sub-pixel accuracy and an automatic determination of the tilt axis. Furthermore, different novel reconstruction algorithms, based on compressed sensing and using neural networks during filtered back projection enabled us to obtain higher quality reconstructions while reducing the number of necessary projection images. Another algorithm that was proposed is the “weighted simultaneous iterative reconstruction technique”, leading to a faster and closer convergence than

conventional methods. Advanced reconstruction algorithms to quantify the 3D composition of nanomaterials were also developed. A novel technique to investigate dopants in nanoparticles was one of our most recent results.

Task 23.2: Atomic Resolution for Nanodevices

At the start of ESTEEM2, high resolution electron tomography was possible for model like systems only. During the project, we extended our work to binary systems, again by using compressed sensing. It is important to note that a very limited number of HAADF-STEM images (4 or 5) is sufficient to obtain a 3D reconstruction in which individual atoms can be visualised. To investigate systems in which atomic scale defects are present, we proposed a novel algorithm that models each atom by a 3D Gaussian function. This methodology enabled us to investigate an Au nanodecahedron. More recently, high resolution electron tomography was used to unravel an unknown crystal structure in which a complex ordering of vacancies is present.

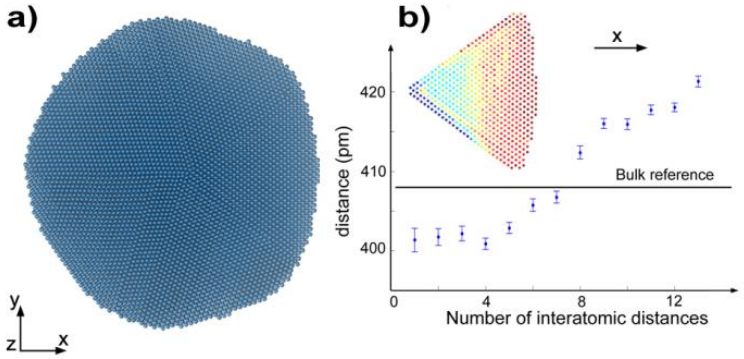


Figure 23.1: a) 3D reconstruction of a Au nanodecahedron with atomic resolution b) Strain field analysis of one of the segments.

Task 23.3: Mapping Fields

The aim of this task was to extend state-of-the-art electron tomography to the investigation of materials properties such as electromagnetic or strain fields. An important advantage of the novel approach developed in Task 23.2 (Figure 23.1) is that the reconstruction yields all atom coordinates as a direct output. In this manner, it becomes straightforward to calculate the 3D displacement map and to investigate strain in 3D as illustrated in Figure 23.1.b. Another highlight in this task was the demonstration of a 3D reconstruction of localised surface plasmon resonances of a Ag nanoparticle. The partners also combined electron holography with electron tomography yielding e.g. a quantitative 3D reconstruction of the dominant axial component of the magnetic induction and electrostatic potential within a cobalt nanowire of 100 nm in diameter with spatial resolution below.

Task 23.4: In Situ 3D Characterisation

Novel TEM holders dedicated to in-situ experiments have been designed. Examples include a holder that allows light irradiation during TEM specimens to enable measurements of current-voltage characteristics and an in-plane-magnetizing specimen holder. Finally, electron beam lithography has been used to make four electrical contacts onto individual self-supporting samples placed into electrical biasing specimen holders. Furthermore, we made use of the algorithms developed in Task 23.2 to estimate 3D morphologies based on a single 2D projection image. In this manner, we were able to visualize changes in the crystal facets of the nanorod as a function of heating.

Task 23.5: Novel Approaches for Tomography

Optical sectioning as well as ptychography was explored as a methodology to obtain 3D information. Although advanced electron microscopy techniques have allowed atomic-scale characterization of edge dislocations from the conventional end-on view, for screw dislocations, the atoms are predominantly displaced parallel to the dislocation line, and therefore the screw displacements are parallel to the electron beam and become invisible

when viewed end-on. Here, optical sectioning using annular dark field imaging in a scanning transmission electron microscope was used to image screw displacements with the dislocation lying in a plane transverse to the electron beam. Because electron ptychography makes use of a convergent beam that can be regarded as an ensemble of plane waves incident over a range of illuminating tilt angles, it inherently contains 3D information. We showed that ~10 nm depth resolution is possible.

Significant results;

Many high impact papers have been published in this JRA including several Nature type publications. These publications are based on the following achievements:

- Development of novel alignment and reconstruction procedures. Many of these procedures are now used by the different partners and other laboratories in the field.
- Development of protocols for high resolution electron tomography which can be applied to complex or unknown (hetero)structures.
- Optical properties, strain and electromagnetic fields have been measured in 3D.
- Holders for in-situ 3D measurements have been successfully developed.
- Optical sectioning and ptychography are valuable alternatives for conventional electron tomography.

Work Package 24: Time resolved TEM

Time-resolved electron diffraction, imaging, and spectroscopy represent a grand challenge for modern electron microscopy, whilst offering a unique opportunity for understanding structural dynamics and the behaviour of matter under conditions away from equilibrium. Gaining knowledge of the dynamical behaviour of (nano)materials and systems requires characterization by tools that can observe structural details in the space scales of micron to angstrom and time scales from femtosecond to milliseconds.

The first approach developed by the EM community was focussed on developing fast detectors able to analyse de dynamical properties of materials in the millisecond range. This was achieved thanks to the development of rapid electronic and high sensitive detectors. Nowadays, new commercial advanced detectors allow acquiring images at rate approaching 400 fps but with limited sensitivity and poor resolution.

To achieve even better time resolution in the femtosecond to nanosecond range, a new type of TEM has been designed by the group of A. Zewail in Caltech (2001). In such pulsed electron microscope, the emission of electrons is triggered thanks to the use of femtosecond laser focussed on a “large” photocathode. These fs lasers assisted pulsed EM however do not allow to perform imaging experiments of high spatial resolution nor electron holography which both require a highly coherent beam.

The aims of this WP were to develop new facilities for dynamical studies in Electron Microscopy focussing on:

- **Fast Transmission Electron Microscopy.** The aim of this task is to design new fast direct electron detectors and read-out electronics, which have large pixel arrays (2048 x 2048), high sensitivity and reasonable speed.
- **Ultrafast coherent Electron Microscopy**. This second task objective is to build a new hybrid time resolved instrument combining a femtosecond laser source and a field emission TEM to create a coherent pulsed beam capable to study in pump/probe experiments ultrafast dynamical processes that occur in nanostructures with nanometre spatial resolution.

Task 24.1 - Fast Transmission Electron Microscopy:

In this task, we developed advanced CMOS detectors with 2048 x 2048 pixels that are fully radiation hardened and which can be used for direct detection without the need for a resolution limiting scintillator and coupling. 12 wafers of sensors have been developed and 4 fully functional radiation hardened sensors at 100um, 50um and 35um thickness and we have constructed all the required readout electronics and mechanical and vacuum interfacing.

The required fast readout and coupling electronics have also been constructed, which enable the sensor data to be acquired across a 100GB Ethernet connection which also provides control of the camera.

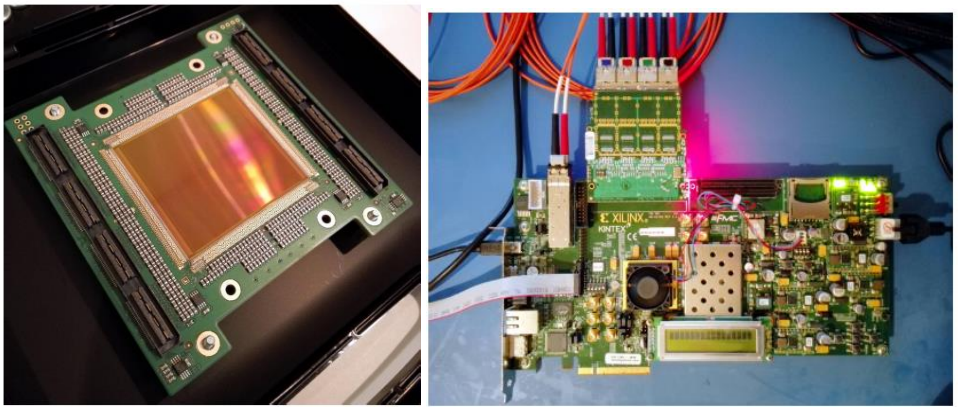


Figure 24.1. Fully functional 2048 x 2048 pixel CMOS imaging sensor thinned to □□0m□ attached to a carrier PCB. Assembled fast readout electronics for data acquisition and camera control.

In a second approach, we have used a Medipix3 sensor designed at CERN and based on commercial 0.13 µm CMOS technology. The sensitive matrix consists of 256x256 pixels at 55µm pitch with an overall area of 15.88 x 14.1 mm^2. This detector can work in Single Pixel Mode (SPM) for in which the count in each pixel in only registered if the deposited energy exceeds a preset lower threshold energy value. This Medipix3 design contains an additional functionality known as Charge Summing Mode (CSM) designed to mitigate the effects of charge sharing. The CSM mode implemented in the Medipix3 detector has been designed to minimize the effect of *charge sharing*. This feature has a significant effect on the MTF and DQE, particularly at lower voltages providing a Modulation Transfer Function (MTF) that is almost invariant with a high Detective Quantum Efficiencies (DQEs). The pixel architecture of the Medipix3 sensor also enables new imaging possibilities. For example, it is possible to acquire images with zero gap time between them, it is also possible to configure the two counters as a single 24-bit counter to access a 1 to 16.7x10^6 dynamic range. This capability directly benefits quantitative recording of diffraction patterns.

Task 24.2 - Ultrafast coherent Electron Microscopy:

We have developed a novel ultrafast TEM allowing generating electron pulses of subpicosecond duration from the interaction of a femtosecond (fs) laser source with a cold field emission (FE) tungsten (310) tip. To achieve such time-resolved electron microscopy experiments in pump-probe mode, we have developed a set-up allowing injecting light on the object within the sample holder part of a HF2000 TEM and a unique fs laser assisted electron gun able to emit coherent electrons on the same HF2000 platform (FemtoTEM). New HV connections, new mechanical parts have been designed, fabricated and installed on the HF2000 TEM column which has in addition been fully equipped with 4Kx4K Gatan detector and a PEELS 666 spectrometer. In parallel, a femtosecond laser source has been installed together with a characterization set-up based on a pulse autocorrelator. An optical set-up has been designed for the alignment of the femtosecond laser source on the metallic nanotip located in the TEM gun together with diagnostic tools and alignment procedure. Generation of 200 keV electrons from the customized field emission gun in DC mode has been demonstrated and a resolution of 1.5 Angstrom has been measured using Young fringes method. The fs laser assisted electron emission has then been carried out and **electron emission in both conventional and laser-driven modes has been obtained**

The light injection device adapted to the HF2000 FemtoTEM microscope has been developed on the base of the design made by the CNRS-LPS. The system is designed for injection from a collimated beam or a point source without loss of spatial coherence, allowing for ultimately diffraction limited spot. The new light injection system has been installed and tested in the FemtoTEM column in CNRS-CEMES. In addition to the injection system, several modifications of the column to accommodate for an imaging system of the injection system when inserted in the HF2000 have been made. A free space light injection system has then been fitted proving the successful light injection and focalization of light in the running FemtoTEM microscope. Simultaneous optical and TEM observation of the nanoparticle destruction by the laser pulse has been done. This experiment confirms that **alignment of electron and laser beam onto the same nano-object inside the objective lens can be routinely achieved inside the FemtoTEM microscope**.

In addition to light injection capabilities, the system allows light detection and therefore time-resolved cathodoluminescence experiments can be performed in this unique FemtoTEM microscope.

Significant results;

- **functioning direct electron detector that operates in several different counting modes has been realized**. The frame rate is ca. 1000fps (limited by data transfer) and we have experimentally demonstrated a dynamic range of 4 orders of magnitude and a near perfect MTF in CSM mode.
- a **unique running fs laser assisted coherent pulsed TEM has been successfully realized:** i.e. the light injection system is working properly (and can be used as detector in cathodoluminescence experiments as well) and the femtosecond laser focused on the tip generates the expected pulsed electron beam. FemtoTEM allows then performing time-resolved TEM experiments in pump-probe mode in the time range of picosecond to nanosecond.

4) Potential impact and the main dissemination activities and exploitation of results

4.1 Potential impact, including the socio-economic impact and the wider societal implication of the project so far

Impact on the European Electron Microscopy workforce

More than 200 people were involved in the implementation of the ESTEEM2 project. Among them, 38 were post-doctoral scientists recruited specifically for the project. These post-docs, trained in the best European laboratories, are the future of Electron Microscopy.

In addition, WP2 was dedicated to the dissemination of expertise in advanced electron based quantitative techniques among the ESTEEM2 members and other European TEM users. Specific objectives were to offer schools and advanced workshops to scientists to enable them to exploit the new possibilities offered by state-of-the-art instruments. The ultimate goal of this activity has been to disseminate knowledge across the European research community which definitely has been achieved. The ESTEEM2 website intends to provide a central repository for reports obtained in this work package, where the website is available at:

http://pmvz-esteem.cemes.fr/index.php/networking-activities/tem-schools-advanced-training-sessions-and-workshops

In total 600 participants – 189 females and 411 males – coming from all over Europe and even from Asia and the Americas have attended these 13 schools and advanced workshops which correspond to an average number of 46 participants per school or workshop. We are strongly convinced that we succeeded in our objectives which were:

- "*… to create new networks of scientists across Europe who are expert in the development and application of advanced TEM techniques applied to specific topical material science issues to underpin considerable academic and industrial activity including semiconductors, catalysts, functional materials and ceramics*."

- "*… to provide of a structured series of schools and workshops which will also encourage young and/or female researchers into this field providing a mechanism for long term sustainability of the EU's leading position in electron microscopy*."

Impact on the European Electron Microscopy Users

Work Packages 3, 4, and 6 have enabled wider access through TA within ESTEEM2 by providing less well equipped European laboratories with the core tools needed for sample preparation and data analysis which are key components of all EM studies. In this regard, it complements the provision of instrumentation through TA.

High-quality protocols for sample preparation

High-quality electron transparent thin film specimens are essential for state-of-the art TEM/STEM investigations. This is why a great effort has been put into optimization of the existing sample preparation techniques, such as tripod polishing, ion milling, FIB techniques, electro-polishing and ultramicrotomy. Two Round-Robin tests conducted by the partners provided important information on reproducibility of samples that were prepared using the same recipe by different laboratories. New techniques for preparing sensitive samples were also investigated. Finally, twenty-two sample preparation protocols were prepared and published as well as publications related to sample preparation which are available to all scientific community using transmission electron microscopy techniques for structural and chemical investigations.

Open-access software

The overarching aim of the WP 4 was to build a European infrastructure for computation and theory to support advanced imaging and spectroscopy. This has been achieved with several novel approaches to the complex calculations required for exit wavefunction reconstruction and spectroscopy in several modes having been developed.

The methods developed have been disseminated not only through the usual academic routes of papers and presentations, but a large number of software modules have been made available to the scientific community free of charge and disseminated with ESTEEM2.

Impact on scientific research

At the end of the project we have counted 498 publications arising from ESTEEM2. However, this is not the final number as many other papers are still in the writing or submission process. It is worth noting that 122 papers are joint publications between ESTEEM2 partners and/or TA user. This shows that the collaboration among the consortium is strong.

Work Package 20: Electron Diffraction

This WP has made an impact both at an academic level and at a wider socio-economic level. The results generated within the WP have led to a string of high quality papers, published in top rank journals, with a wide readership and broad appeal. Some of the published work has been followed up by shorter popular articles. A significant component of the work has been in software development and code developed in the WP is open source.

Work Package 21: Imaging

The overarching aim of the work package was to build a European infrastructure to enable transmission electron microscopy to provide quantitative measurements of materials at atomic resolution. This has been achieved through: (i) Building an understanding of the appropriate technique for a specific measurement. (ii) The development of new experimental techniques to enable measurements to be made of parameters that were not possible previously, or from samples that could not be examined previously. An example of this is the development of ptychography using fast pixelated detectors to observe the widest possible range of elements in a sample. (iii) Calibration and data inversion methods to allow measurements, and importantly the precision of the measurements, to be determined. An example of this is the application of statistical parameter estimation theory.

The methods developed have been disseminated not only through the usual academic routes of papers and presentations, but a large number of software modules have been made available to the scientific community free of charge, as described in the periodic reports.

Work Package 22: New types of electron spectroscopy

This WP has directly impacted its related fundamental research field, as emphasized by the quantity of papers published in highly ranked journal (1 Nature, 1 Nature Physics, tens of papers in PRL or Nanoletters…), several of them being “highly cited” papers in ISI web of science and “first” in their own fields (see “highlights”). Software developments in this WP are free and/or open source. A large majority of the works made in tasks 22.2 and 22.3 concern materials of technological interest for electronics, spintronics, oxytronics, multiferroic, solid state lighting materials, quantum coherent technology or of environmental/energy interest (photovoltaics, geomaterials…). Patents related to instrumental developments have been issued. Finally, methodological developments have started to be applied to biological applications.

Work Package 23: 3D nanometrology

To obtain full control over the physical properties of nanostructures, it is necessary to understand the connection between properties and atomic structure/composition. To model such interactions, ab-initio calculations can be performed, which require detailed and quantitative information as an input. In the past, TEM investigations were often based on 2D projection images of 3D objects and especially for nanostructures, this can certainly yield misleading or incomplete results. Since the start of ESTEEM2, electron tomography has evolved from a technique to visualize the morphology of (nano)materials to a quantitative technique to measure the 3D structure and properties (magnetic, optical) of nanomaterials.

Work Package 24: Time-resolved electron microscopy

The incomparable combination high spatial resolution (few ten of picometers) and energy resolution (few tens of meV) of TEM associated to advanced techniques like precession electron diffraction, electron tomography, electron holography, *in-situ* TEM experiments… make TEM an essential tool for the academic and industrial researches for the advanced (3D) structural and chemical characterization of (nano)materials and devices that could be even studied *in operando*. The next major scientific topic TEM has to tackle is to perform these studies as function of time to perform dynamical TEM studies keeping the same spatial and energy resolutions.

The instrumental developments that have been successfully achieved within this WP offer the capability for TEM to study time dependant phenomena in Materials Science. The impact of such time-resolved TEM capabilities is huge. The developments of *in-situ* experiments, which allow the study of materials and devices *in operando* require the use of fast detectors being able to follow the processes at the appropriate time scale. As example, in environmental TEM experiments performed on catalysis nanoparticles under various atmosphere and temperature conditions, the changes of the local structure and composition of the nanoparticles have to be recorded with sufficiently fast and sensitive detectors. This is also a requirement for the study of the plasticity behaviour of structural (nano)materials submitted to external stress for applications as structural elements. The complete characterization of domain motion in magnetic or ferroelectric materials when submitted to an external magnetic or electric field is also of huge interest for applications and requires the use of fast sensitive detectors as the ones developed within this WP.

Ultrafast pulsed TEM with picosecond to nanosecond time resolution in pump probe experiment will also have a large impact in the dynamical studies of reversible phenomena occurring in Physics and Material Science. As examples, the studies of the dynamical optical properties of materials, in particular plasmonics, will surely benefit of these developments with potential application in new opto-electronic devices, the understanding of the local dynamical properties of nanomagnetic materials should open a new route in spintronics and magnetic data storage. The time resolved studies of phase transitions should bring valuable information regarding local behaviour at the nanometre scale of 1st order and 2nd order phase transitions. The study of strain in various materials should as well be lighted when having access to the dynamical properties of the deformation propagation mode.

We argue that the time-resolved TEM developments achieved within the ESTEEM2 project will pave the way for future research in a huge number of time-dependent phenomena by this unique combination of spatial, energy and time resolutions.

Economic impact

The WP20 (diffraction) has been wide-ranging in its investigation of different materials with a spectrum of uses and applications. These include Ni-base superalloys, for next-generation turbines and engines, semiconductor nanostructures with novel electronic properties and uses, organic semiconductors for use in flexible opto-electronic applications. We have also developed techniques applicable to the life sciences with the possibility of applying scanning electron diffraction methods to organic crystals including pharmaceutical compounds and even protein crystals.

The new capabilities enabled by WP21 (Imaging) enable research in materials that have a wide range of social and economic importance. Examples include the study of catalysts for hydrogen fuel cell applications and energy storage using Li and Na ion technologies. Collaborations with industry in both these areas have led to samples to which the infrastructure developed here has been applied. In addition, there has been engagement with European instrument suppliers as part of this research. CEOS GmbH, an SME based in Heidelberg, has been a partner in the use of aberration correction techniques. In addition, the work on the use of fast pixelated detectors has been conducted in collaboration with PNDetector GmbH, an SME based in Munich.

A large majority of the work in tasks 22.2 and 22.3 concern materials of technological interest for electronics, spintronics, oxytronics, multiferroic, solid state lighting materials, quantum coherent technology or of environmental/energy interest (photovoltaics, geomaterials…). Patents related to instrumental developments have been issued. Finally, methodological developments have started to be applied to biological applications.

Tools developed in WP23 (3D nanometrology) are of great importance. For example in semiconductor industry, characterisation of device morphology should be complemented by 3D electromagnetic fields and strain maps. Also catalytic nanoparticles play an important role in our current industry; the ability to determine the active atomic sites at their surface has an enormous impact. The information that will follow from the novel 3D reconstruction tools will not only have fundamental, but also great technological impact as it will lead to the optimisation of the current synthesis techniques and the design of novel nanostructures with predefined functionalities.

4.2 Dissemination activities and exploitation of results

Dissemination activities of ESTEEM2 were mainly carried out in the Work-Package 5. The main objective of this WP was to ensure the largest promotion of the ESTEEM2 activities and TA opportunities to four different types of audiences:

- Electron microscopy scientists outside the network
- All scientists that could make use of Electron Microscopy for their research
- Companies that manufacture components for Electron Microscopy
- Companies that use Electron Microscopy to develop new products

The ESTEEM2 website (http://esteem2.eu) was the main tool to address any kind of audience, as it contains all information regarding the project activities, the installations available and the submission of user-projects.

In addition, several promotion documents were edited during the project:

- A brochure was created at the beginning of the project for the promotion of ESTEEM2 capabilities, particularly regarding TA.
- We have composed a comprehensive booklet (62 pages, 750 prints) with title: ***"Advanced Capabilities in Transmission Electron Microscopy. Opportunities for Materials Science and Industry in Europe"***. This booklet not only introduces the different partners involved, but it particularly illustrates the materials science problems that can be solved and is expected to be used by industrials facing to an issue of material science type.
- A brochure summarizing the achievements made during the four years of ESTEEM2 was edited. Hard copies are currently sent to the Electron Microscopy stakeholders that we have identified: the European Commission, National Funding Agencies representatives, and Companies that have demonstrated their interest for the EM technology and for the project.
- Disseminating information towards scientific communities outside the electron microscopy community was also ensured through the publication of an advert in Nature Nanotechnology and Nature Physics journals, and an article about ESTEEM1&2 in Comptes Rendus Physique.
- Finally, a paper highlighting ESTEEM2 will soon be published online in the DG research success stories website (https://ec.europa.eu/research/infocentre/success_stories_en.cfm). The content of the article was discussed with the RETELL agency, which has already submitted the article to the DG research.

An ESTEEM2 group was created on LinkedIn (https://www.linkedin.com/groups/8464679) that gathers now 225 members. The group includes electron microscopists coming from ESTEEM2 partners' institutions or other laboratories (in Europe and abroad), electron microscopy experts from the industrial sector and officials from the European Commission and national research ministries.

Direct promotion of the project was also ensured by all members of the consortium at numerous conferences (task 5.4) and by JSI Ljubljana and AGH Krakow to promote TA towards New Member States Users (task 5.7).

Significant results

- From 25th June 2013 to 30th September 2016 the website has received 15148 visits.
- Newsletters can be found on the website and they are also sent to the participating laboratories as well as TA users and potential users (about 220 contacts).
- We have produced a comprehensive booklet: *"Advanced Capabilities in Transmission Electron Microscopy. Opportunities for Materials Science and Industry in Europe"*. This booklet introduces the different partners, but it particularly illustrates the materials science problems that can be solved. It was distributed to more than 200 companies operating in the field of nanotechnology.
- A brochure highlighting ESTEEM2 achievements was edited and sent to national funding agencies, the European Commission, and other relevant stakeholders
- An ESTEEM2 group was created on Linked, which gathers already 225 people
- An article about ESTEEM2 was approved by the RETELL agency (sub-contractor of the DG RTD for publication of success stories) and will soon be published online

Wider engagement with society

Atomic resolution electron microscope images are a remarkable view of nature, and are an excellent tool to enable wider public engagement in science. Many of the partners in WP21 have used their electron microscopy capabilities for public outreach activities. For example, the UOXF capabilities have been used to allow school students from the Northwest Science Network, an outreach activity based in socio-economically less developed regions in the northwest of England, to operate a microscope for themselves and "see atoms".

Other original initiatives were supported by the members of ESTEEM2, for example UCA members took part in the organization and development of the Science Communication Activities carried out during The Tall Ships Races Cadiz 2016, which took place in Cadiz in July 2016. These activities were open to the general public and more than 2000 visitors participated in the Science Communication activities (http://regatacadiz2016.es/). In particular, the NanoWorld Workshop was dedicated to introduce the nanometric and atomic scale to the participants, showing examples of nanometric materials and introducing electron microscopy techniques.

Another example is the movie realised by the Research Infrastructure Consortium of NCPs (RICH) for its series entitled "Portraits of Research Infrastructures": http://www.rich2020.eu/rich-videos. This short video follows the Prof. Franco Rustichelli (UNIPVM, Ancona), an ESTEEM2 TA user, during his visit to AGH Krakow.

5) Public website and relevant contact details

The ESTEEM2 website is available at: esteem2.eu

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