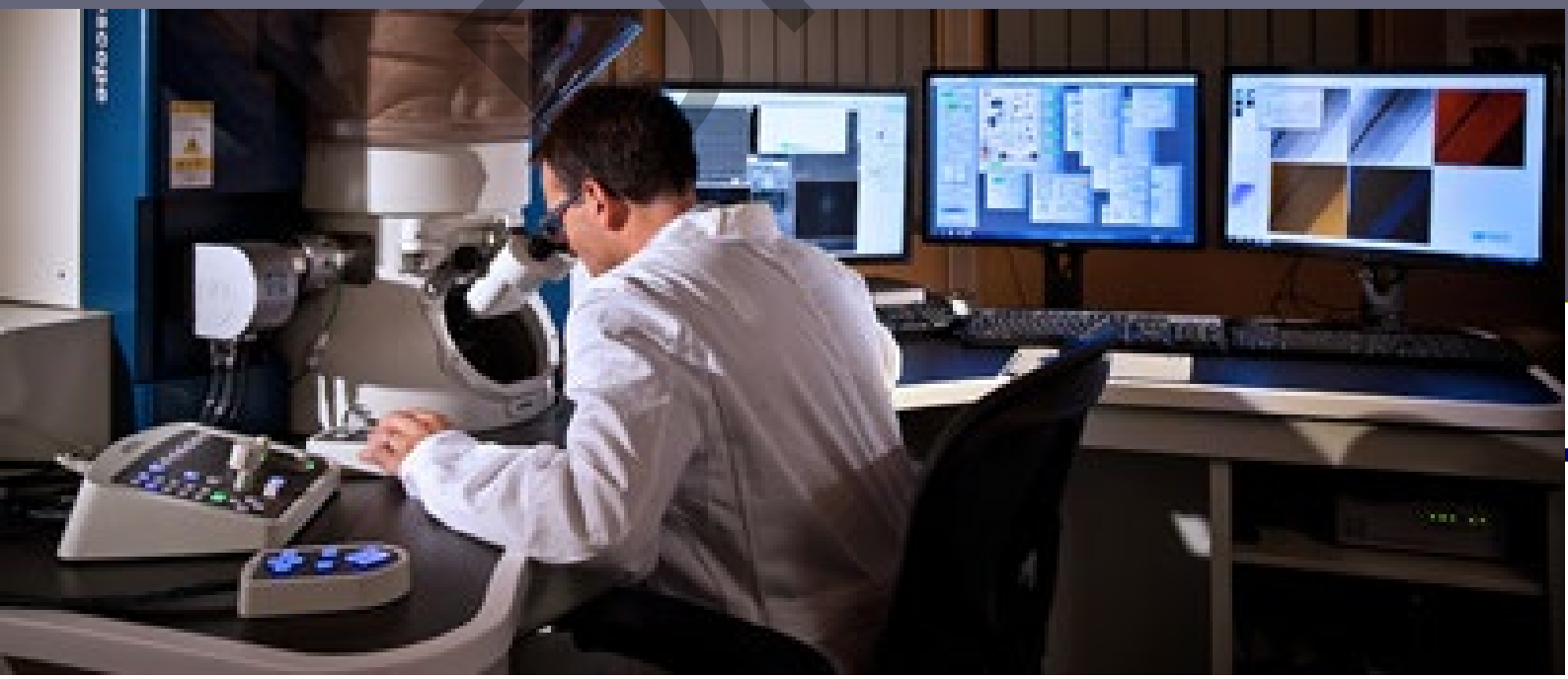
esteem3

Enabling Science through European Electron Microscopy

Report on evaluation of precision estimates for TEM experiments

Deliverable D4.6- V1.2

Estimated delivery date:	30/04/2023
Actual delivery date:	04/05/2023
Lead beneficiary:	CNRS
Person responsible:	Martin Hytch
Deliverable type:	☒ R ☐ DEM ☐ DEC ☐ OTHER ☐ ETHICS ☐ ORDP
Dissemination level:	☒ PU ☐ CO ☐ EU-RES ☐ EU-CON ☐ EU-SEC



THIS PROJECT HAS RECEIVED FUNDING FROM THE EUROPEAN UNION'S HORIZON 2020 RESEARCH AND INNOVATION PROGRAMME UNDER GRANT AGREEMENT NO **823717**

Grant Agreement No:	823717
Funding Instrument:	Research and Innovation Actions (RIA)
Funded under:	H2020-INFRAIA-2018-1: Integrating Activities for Advanced Communities
Starting date:	01.01.2019
Duration:	54 months

Table of contents

Revision history log

Version number	Date of release	Author	Summary of changes
V0.1	27.04.2023	Martin Hytch	First draft of deliverable
V0.2			Feedback from partners- UANTWERP, JUELICH, UOXF
V1.0	05.05.2023	Peter van Aken	Minor amendments and approval
V1.1	05.05.2023	Aude Garsès	Minor amendments and final review

Introduction

Modern TEM instruments provide a wealth of information from nanoscale samples with atomic spatial resolution. For quantitative measurements, however, there is a clear need for improved accuracy, precision and reproducibility. Instrumental advances are important in this respect, such as the development of aberration correctors and direct electron detectors through their improved performance. Furthermore, new instrumentation creates opportunities to develop new methods in imaging and diffraction. In turn, this creates corresponding demands in metrology, which is the subject of this report. Novel calibration procedures have already been the subject of a previous report (D4.4) so here, we concentrate on the estimation of the precision and accuracy of the measurement. The methodology is linked to the desire to minimise the electron dose (D4.3).

The methodology for estimating the precision and accuracy of measurements was established in ESTEEM1 using model-based quantification. A realistic model for the experiment must be developed and compared to the experimental data, the statistics concerning the electron dose and specimen variability allowing an estimate of the precision. During ESTEEM3, different aspects of this procedure have been analysed and developed, including automated fitting procedures, better evaluation of specimen preparation artefacts and the combination of more than one experimental signal in the analysis.

Precision in charge-counting experiments

Electron holography is an eminently quantitative technique and can be used to measure magnetic, electric and even strain fields, as has been largely developed during ESTEEM1 and ESTEEM2. During ESTEEM3, the precision of charge measurements has been improved, notably with the introduction of in-situ biasing experiments (see D6.1) and automation (D11.3). The methodology has also been improved by including model-based fitting of experimental data. Figure 1 shows the setup in JUL for measuring the charge on nanowires [1].

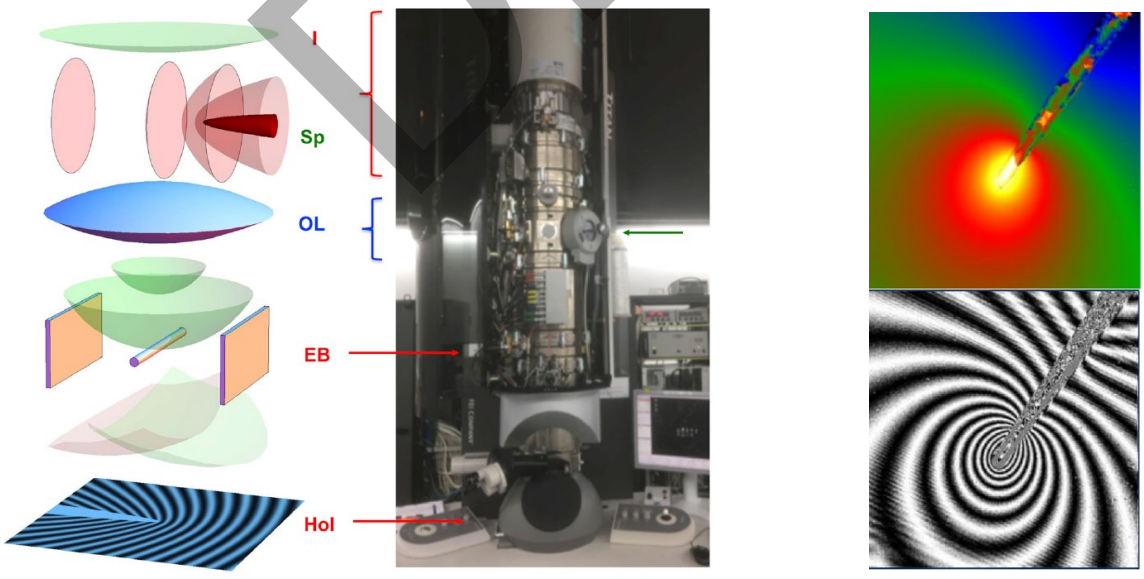


Figure 1. Off-axis electron holography setup for in-situ biasing experiments of nanowires (JUL), from [1], with accompanying phase and cosine-phase image of biased nanowire, from [2].

Parameters that can affect charge density measurements include the mean-inner potential (MIP) contribution to the phase, the spatial resolution of the recorded phase image, its signal-to-noise ratio

(SNR), strong diffraction conditions (which can affect the measurement of the MIP contribution to the phase), electron-beam-induced specimen charging effects and the influence of sample imperfections (e.g., damage, contamination, and oxidation). Importantly, the advent of in-situ biasing has allowed static effects to be removed from the data. A hologram is acquired whilst grounding both electrodes and used as a reference for subsequent holograms whilst biasing [3,4]. The procedure greatly improves the accuracy of the measurements by the removal of systematic errors.

The local charge density can, in principle, be determined directly from the electric potential, and hence the phase of the electron hologram, through Gauss's Law. However, there are several different ways of proceeding, such as: an analytical model-dependent approach, in which a mathematical model is used to describe the charge density and phase shift; a model-independent approach, which is based on the application of a Laplacian operator to a recorded phase image; and a model-based iterative reconstruction approach, in which the charge density in a forward model used to simulate phase images is varied until a best match to the experimental measurements is obtained [1]. Each method has been applied to the test case of a charged nanotip. It was found that whilst results were consistent, the model-based iterative approach gave the highest precision.

A similar approach was applied to the analysis of nanocapacitors, but with the electric potential modelled using the finite element method [3]. This allowed the influence of the TEM specimen geometry and stray fields to be thoroughly evaluated. By comparing the simulations with the experimental phase profiles, the electrical potential within the sample could be determined. In particular, layers of charge were revealed at the interface of the insulator with the electrodes. The charge density was determined as a function of the applied bias and the precision estimated by careful analysis or the possible sources of error. This experiment benefited from dynamic automation stabilising the specimen position and hologram fringe position.

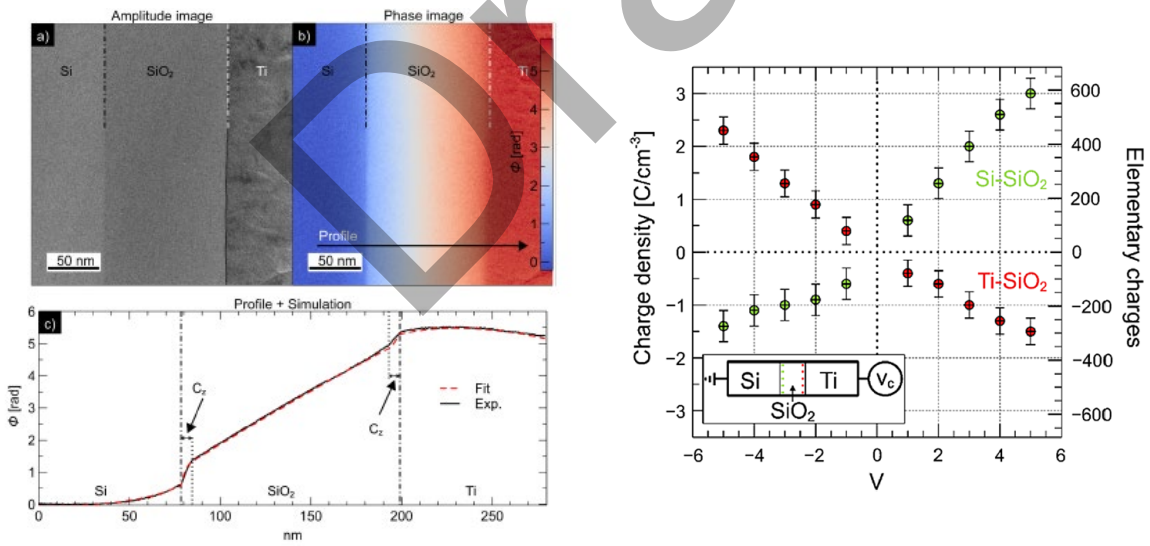


Figure 2. Automated *operando* electron holography of a MOS nanocapacitor: (a) amplitude of holographic fringes showing specimen geometry; (b) phase shift caused by biasing; (c) experimental phase profile averaged along 100 nm of interface and simulated profile from finite-element method modelling; (d) charge density at Si-SiO_2 and Ti-SiO_2 electrode-oxide interfaces. From [3].

The approach was further applied to a working device from a leading European semiconductor company [4]. Since the charge can be measured, the capacitance of the device can be estimated assuming the dielectric properties of the insulating layer. The results can then be compared to electrical measurements carried out on site as part of quality control.

The precision in such experiments can reach one elementary charge but will depend on spatial resolution and the type of specimen. The highest precision can be obtained for measuring the total charge on a nanoparticle or nanowire radiating electric field into the surrounding vacuum [1,2]. In such cases, the phase of the electron hologram is measured in vacuum, where the signal-to-noise ratio is the highest, and the area of analysis can be very large, much larger than the nanotip or particle. In principle, the whole region of vacuum within the field of view can contribute the measured signal. A more challenging situation is the measurement of the local charge density within a specimen [3,4]. In such cases, the best current precision is of the order of 50 elementary charges with a resolution of 0.8 nm in the growth direction and averaged over 100 nm parallel to the interface [3]. Nevertheless, this allows the measurement of interface charge densities of as little as 0.3 μC·cm-2.

Precision in atom counting experiments

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) is a technique that, when used wisely, produces images of incomparable clarity at the atomic scale. The intensity of the atomic contrast depends monotonically on the number of similar atoms in the corresponding column. Throughout ESTEEM2 and ESTEEM3, the model-based analysis of the contrast has been developed to count the number of atoms in individual atom columns, notably in nanocrystals (Figure 3).

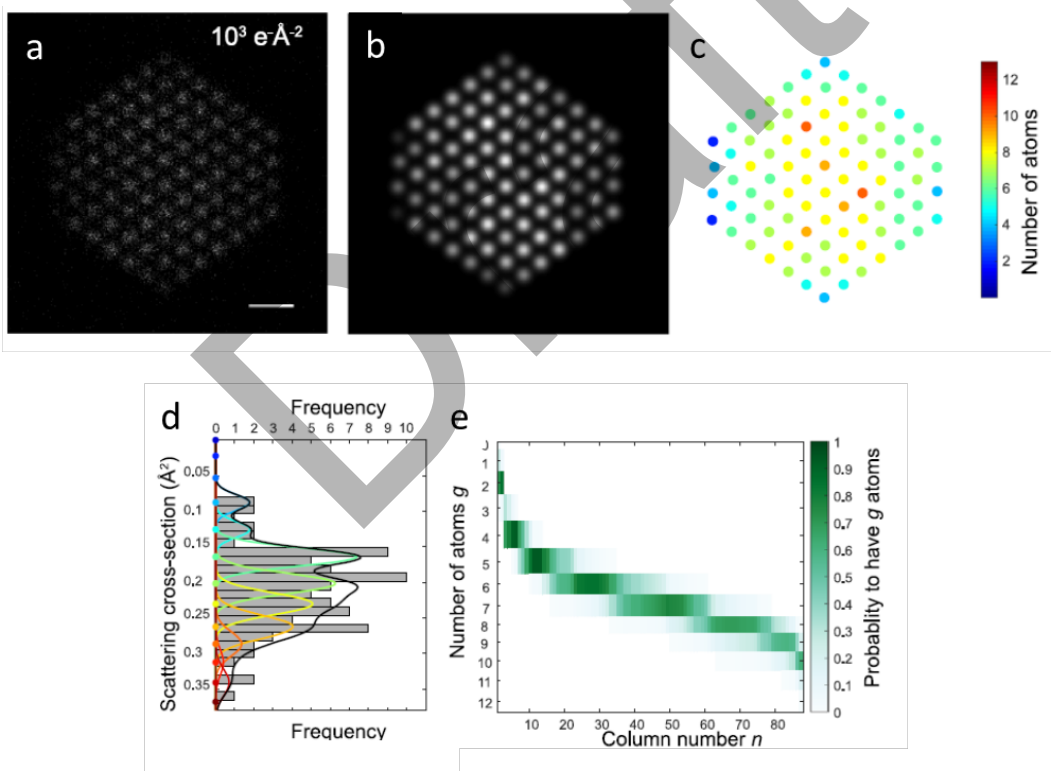


Figure 3. Model-based atom counting: (a) simulated HAADF-STEM image of a Pt nanoparticle; (b) refined parametric model; (c) corresponding number of atoms in each column; (d) scattering cross-sections; (e) probability distributions. From [5].

In ESTEEM3, the methodology has been refined by including Bayesian theory to calculate the probability distribution of a particular column having a certain number of atoms [5].

Precision can be improved by correlating information from different signals. This has been done for atom counting using HAADF-STEM and EDX data collected simultaneously [6]. The technique is particularly useful in low-dose conditions (see D4.3).

Conclusions

Quantitative electron microscopy began by trying to quantify the experimental image and determine microscope parameters. Now, the methodology has been developed to determine specimen-related parameters and physical quantities such as the number of charges and atoms in a sample. The precision of a single elementary charge and a single atom has been achieved. Progress has been made to attain similar precision for working devices and low-dose conditions.

[1] F. Zheng, J. Caron, V. Migunov, M. Beleggia, G. Pozzi, R. E. Dunin-Borkowski, Journal of Electron Spectroscopy and Related Phenomena 241, 146881 (2020). *Measurement of charge density in nanoscale materials using off-axis electron holography*. 10.1016/j.elspec.2019.07.002

[2] F. Zheng, M. Beleggia, V. Migunov, G. Pozzi, R. E. Dunin-Borkowski, Ultramicroscopy 241, 113593 (2022). *Electron-beam-induced charging of an Al_2O_3 nanotip studied using off-axis electron holography*. 10.1016/j.ultramic.2022.113593.

[3] M. Brodovoi, K. Gruel, A. Masseboeuf, L. Chapuis, M. Hÿtch, F. Lorut, and C. Gatel, Appl. Phys. Lett. 120, 233501 (2022). *Mapping electric fields in real nanodevices by operando electron holography*. *10.1063/5.0092019, hal-03752638*

[4] C. Gatel, R. Serra, K. Gruel, A. Masseboeuf, L. Chapuis, R. Cours, L. Zhang, B. Warot-Fonrose, and M. J. Hÿtch, Phys. Rev. Lett. 129, 137701 (2022). *Extended charge layers in metal-oxide-semiconductor nanocapacitors revealed by operando electron holography.* 10.1103/PhysRevLett.129.137701, hal-03787333

[5] A. De Backer, S. Van Aert, C. Faes, E. Arslan Irmak, P. D. Nellist and L. Jones, NPJ Computational Materials 8, 216 (2022), *Experimental reconstructions of 3D atomic structures from electron microscopy images using a Bayesian genetic algorithm*. 10.1038/s41524-022-00900-w

[6] A. De Backer, Z. Zhang, K. H.W. van den Bos, E. Bladt, A. Sánchez-Iglesias, L. M. Liz-Marzán, P. D. Nellist, S. Bals, and S. Van Aert, Small Methods 6, 2200875 (2022), *Element Specific Atom Counting at the Atomic Scale by Combining High Angle Annular Dark Field Scanning Transmission Electron Microscopy and Energy Dispersive X-ray Spectroscopy*. 10.1002/smtd.202200875